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**METHODS FOR ASSESSING DEGRADING EFFECTS
OF UV RADIATION ON MATERIALS**

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Abstract

UV radiation is one of the key factors ageing materials and thus limiting their service life time. Damages induced by UV radiation may be observed as changes in the properties of the material. Various types of weathering experiments are used to study the chemical and physical mechanisms behind the degradation process. Material samples are exposed to UV radiation and other environmental stress agents in natural outdoor and artificial conditions in laboratory. Quantification of the material's response to the exposure yields knowledge on the ageing behaviour of the material. This knowledge is essential when selecting materials to comply with the service requirements, as well as developing materials with extended durability.

The focus of this study has been on certain methods used in investigation of the deleterious effects of UV radiation on materials. Various aspects of weathering and analysis of material property changes are considered. As regards weathering, three main topics unfold: sampling of data from outdoor weathering experiments; construction of continuous time series of UV radiation exposures over the weathering periods; and comparability of artificial UV radiation conditions to those encountered under the Sun. Within the scope of the property change analysis, the study has focused on the wavelength dependencies found in damage induction.

A new method is proposed for planning the timetable of a natural outdoor weathering experiment in a way that the seasonal and geographical variations are accounted for. The method simplifies the post-exposure analysis of the material properties and improves the comparability of test results obtained at different weathering sites. A new approach is adopted to reconstruct the solar spectral UV irradiance at the Earth's surface through radiative transfer modelling. The method provides a means for deriving UV irradiance in cases where no direct measurements of the quantity are available. As a result, a continuous UV radiation time series is obtained, as required for the determination of the UV radiation exposure accumulated on the materials. To improve the comparability of accelerated ageing to that naturally occurring outdoors, a method for characterizing the UV radiation conditions used in a UV chamber is presented. Knowledge on the exposure is further used to establish a correlation between the artificial and natural ageing environments, facilitating predictions on how the materials would survive in their real service environments.

The study aiming at improvements in the analysis of material property changes is two-fold. A novel facility designed and constructed for exposing materials with spectrally resolved UV radiation is reported. The instrument opens new pathways for the investigations on wavelength specific damages in materials. The facility has been exploited in a study on the wavelength sensitivity of newspaper to photoyellowing. A new approach in deriving the action spectrum of photoyellowing of a material is proposed. The resulting action spectrum may be used in optimizing the chemical and/or physical protection of the material against UV radiation.

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Menetelmiä UV-säteilyn materiaaleja vanhentavien vaikutusten arviointiin

Tiivistelmä

UV-säteily on yksi merkittävimmistä materiaaleja vanhentavista tekijöistä. UV-säteilyn aiheuttamat vauriot voidaan havaita materiaaleissa ominaisuusmuutoksina. Vanhenemisprosessin taustalla olevien kemiallisten ja fysikaalisten mekanismien tutkimiseen käytetään erilaisia säätestausmenetelmiä. Materiaalinäytteitä altistetaan UV-säteilylle ja muille ympäristötekijöille luonnonoloissa ja keinotekoisesti luoduissa olosuhteissa laboratoriossa. Materiaalin vanhenemiskäyttäytymisestä saadaan tietoa määrittämällä, kuinka materiaali vastaa siihen kohdistettuun altistukseen. Tämä tieto on oleellista valittaessa käyttökohteisiin sopivia materiaaleja ja kehitettäessä uusia, entistä kestävämpiä materiaaleja.

Tässä työssä on keskitytty menetelmiin, joita käytetään tutkittaessa UV-säteilyn materiaaleille haitallisia vaikutuksia. Tarkastelun erityiskohteet ovat valikoituneet säätestauksen ja materiaalien ominaisuusmuutosten tutkimuksen piiristä. Säätestauksen osalta on käsitelty kolmea aihetta: materiaalien ulkoaltistustesteissä käytettävää näyteistystä; jatkuvien aikasarjojen rekonstruointia altistusjaksojen aikana vallinneelle UV-säteilykuormalle; ja keinotekoisien UV-altistusympäristöjen vertailtavuutta todelliseen auringon säteilystä saatavaan altistukseen. Materiaalien ominaisuusmuutosten tutkimisen osalta työn keskiössä ovat olleet materiaalien vaurioitumisherkkyksien riippuvuudet altistavan UV-säteilyn aallonpituudesta.

Työssä esitetään menetelmä materiaalien ulkotestien aikataulun suunnittelemiseksi tavalla, joka huomioi UV-säteilyn ajalliset ja paikalliset vaihtelut. Menetelmän soveltaminen yksinkertaistaa altistuksen jälkeistä materiaalien ominaisuusmuutosten analyysia ja parantaa eri paikoissa ja eri aikoina suoritettujen ulkotestien tulosten keskinäistä vertailtavuutta. Altistuksen aikana vallinneen UV-säteilykuorman määrittämiseen on kehitetty säteilykuljetusmalliin pohjautuva menetelmä. Menetelmän avulla voidaan rekonstruoida jatkuva UV-säteilyn irradianssin aikasarja, jota tarvitaan määrittäessä altistuksen aikana testimateriaaleille kumuloinut UV-säteilyrasitus. Keino-oloissa ja luonnonoloissa havaittavien vanhenemismekanismien vertailtavuuden lisäämiseksi esitetään menetelmä laboratoriolaitteen tuottaman UV-altistuksen karakterisointiin. Tietoa on edelleen käytetty määrittämään keino-olot ja luonnonolot toisiinsa suhteuttava korrelaatio, joka mahdollistaa käyttöympäristössä pätevän materiaalin eliniän ennustamisen.

Materiaalien ominaisuusmuutoksia tarkasteleva tutkimus on kaksiosainen. Työssä esitellään uusi laitteisto, joka on rakennettu materiaalien altistamiseksi spektrisesti erotellulla UV-säteilyllä. Laitteisto avaa uusia mahdollisuuksia materiaalien vaurioitumisherkkyden aallonpituusriippuvuuksien selvittämiseen. Laitteistoa on käytetty sanomalehtipaperin kellastumisen aallonpituusriippuvuuden tutkimiseen. Työssä on kehitetty uudenlainen tapa määrittää kellastumisen vaikutusspektri. Tietämystä materiaalien vaikutusspektreistä voidaan hyödyntää muun muassa materiaalien optimaalisen UV-säteilynsuojauksen kehittämisessä.

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Preface

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Helsinki, 9 September 2014

Anu Heikkilä

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- II Lindfors, A., Heikkilä, A., Kaurola, J., Koskela, T. & Lakkala, K. 2009, "Reconstruction of Solar Spectral Surface UV Irradiances Using Radiative Transfer Simulations", *Photochemistry and photobiology*, vol. 85, no. 5, pp. 1233-1239.
- III Heikkilä, A., Kärhä, P., Tanskanen, A., Kaunismaa, M., Koskela, T., Kaurola, J., Ture, T. & Syrjälä, S. 2009, "Characterizing a UV chamber with mercury lamps for assessment of comparability to natural UV conditions", *Polymer Testing*, vol. 28, no. 1, pp. 57-65.
- IV Kärhä, P., Heikkilä, A., Ruokolainen, K. & Kaunismaa, M. 2011, "A novel facility for ageing materials with narrow-band ultraviolet radiation exposure", *Review of Scientific Instruments*, vol. 82, no. 2, pp. 023107.
- V Heikkilä, A. & Kärhä, P. 2014, "Photoyellowing revisited: Determination of action spectra independent from intensity and duration of UV exposure", *Polymer Degradation and Stability*, vol. 99, pp. 190-195.

In Paper I, Heikkilä is responsible for the development of the method presented, the analysis of the performance of the method, and the writing of the manuscript.

In Paper II, Heikkilä carried out the statistical analysis and shared the writing of the manuscript with the leading author.

In Paper III, Heikkilä is responsible for the measurements, the development of the method, and the writing of the manuscript.

In Paper IV, Heikkilä contributed to the characterization of the experimental set-up and the analysis of the data, and shared the writing of the manuscript with the leading author.

The responsibility of the method presented in Paper V is shared by Heikkilä and the co-author. Heikkilä is responsible for the analysis of the performance of the method and the writing of the manuscript.

1 Introduction

Ultraviolet (UV) radiation is electromagnetic radiation that covers the range of wavelengths (commonly denoted by symbol λ) from 100 nm to 400 nm. The wavelength band of UV may be further divided into three subbands: UV-C ($100 \text{ nm} \leq \lambda < 280 \text{ nm}$), UV-B ($280 \text{ nm} \leq \lambda < 315 \text{ nm}$), and UV-A ($315 \text{ nm} \leq \lambda < 400 \text{ nm}$). The wavelength range $10 \text{ nm} \leq \lambda < 121 \text{ nm}$ is considered extreme UV radiation (EUV) (ISO 21348). All bands of UV radiation may be found in the spectrum of the Sun. However, the atmosphere of the Earth effectively absorbs radiation with wavelengths shorter than approximately 280 nm. Therefore, in the solar spectrum at the Earth's surface, only UV radiation with wavelengths on the bands of UV-B and UV-A are detected (e.g., Liou, 2002).

UV radiation is energetic enough to affect many materials, specifically those consisting of polymers (Andrady et al., 1998). Like all electromagnetic radiation, UV radiation is composed of photons that carry energy inversely proportional to the wavelength. The level of photon energies in UV radiation is often high enough to initiate changes in the structure of the material it encounters. It is the consequence of these structural changes that manifest in deterioration, also called weathering, of materials: something we may witness in our everyday lives, watching our plastics to fade, acrylates to brittle, papers to yellow, and rubbers to perish. Essentially, the phenomenon sets the limits for the service life times of many commodities, both consumables and durable goods.

Most often, degradation is a result of joint effects of several weathering factors, including factors like heat, moisture, precipitation, and solar radiation, but also pollutants like soot, acid rain and ozone, and bio-factors such as pollen, fungi and mould. The joint effect of various factors appears often synergistic, i.e., the effect of several factors is more than just a sum of the effects caused by the individual factors (Rabek, 1995). Separation of different factors in material degradation is a complicated task. UV radiation is nevertheless found to be the key factor initiating or significantly contributing to the process of degradation. In fact, UV radiation is currently considered the most significant ageing factor for most materials (Wypych & Faulkner, 1999).

Investigations on weathering of materials commonly employ a two-phase procedure (Searle, 2003). In the first phase, material samples are exposed to the weathering agents. In the second phase, post-exposure material tests are applied to examine the property changes caused by the weathering. In natural outdoor weathering, the first phase means exposing the samples to the natural environmental stress agents on a selected geographical location over pre-defined periods of time. In artificial weathering, material specimens are exposed to weathering agents like UV radiation, heat, and water spray, generated by man-made laboratory equipment. After exposing the samples, they are examined for the changes in their properties. In addition to visual evaluation, a range of test methods is employed to quantify the degree of deterioration (Brown, 1999).

Standardized procedures have been developed to give coherence to the conduction of both natural and artificial weathering of materials (e.g., Boxhammer, 1999; McGreer, 2001; Searle, 2003). Current state-of-the-art uses high quality instrumentation in monitoring the weathering circumstances as well as in post-exposure testing of the weathered materials. However, it is acknowledged that many approaches and methods currently in use would deserve and benefit from re-evaluation and/or further development (e.g., Karbhari, 2001). These aspects gather from the whole field of the discipline: weathering and post-exposure testing, theoretical considerations and experimental designs alike.

In this thesis, improvements in methods for assessing the degrading effects of UV radiation on materials are suggested. The improvements are related to the following aspects of investigation: Timing of outdoor weathering experiments; characterization of equipment used in exposing materials with artificial UV radiation; derivation of UV exposure accumulated on outdoor materials over defined weathering periods; investigation of material specific wavelength dependencies in the sensitivity of degrading materials; and determination of the action spectrum describing the progress of a property change in the degrading material.

The thesis consists of five original papers, numbered as indicated above in the list of the original publications, and hereinafter referred to as Papers I-V. Each paper deals with a different aspect of the topic. However, every paper can be identified as a facet cross-linked to the others, forming a set of methods that can be used in pursuing more valid assessment on the weathering resistance of materials against UV radiation.

Paper I suggests a method for planning the timetable of a natural outdoor weathering experiment in a way that the seasonal and geographical variations are accounted for. The method uses a priori knowledge on the average annual cycle of UV irradiance, retrieved from the measurements made by an instrument onboard a satellite passing regularly over the weathering site. The method simplifies the post-exposure analysis of the material properties and improves the comparability of test results obtained at different weathering sites.

Paper II presents a method to reconstruct the spectrum of the solar UV radiation at the Earth's surface on the basis of radiative transfer modeling. The method provides a means for deriving UV irradiance in cases where no direct measurements of the quantity are available. For weathering experiments, this makes it possible to compute the UV irradiance levels for the occasions with missing measured data. As a result, a continuous UV radiation time series is obtained, as required for the determination of the UV radiation exposure accumulated on the materials.

In Paper III, a method for characterizing the UV radiation conditions used in accelerated ageing of materials is presented. The method provides a way to quantify the UV radiation exposure on the samples aged for a defined period of time. Knowledge on the exposure is a pre-requisite in any attempt to correlate the artificial ageing conditions to those naturally prevailing outdoors. Once derived, the correlations facilitate predictions on how the materials would survive in their service environments on the basis of the degradation observed in the laboratory.

Paper IV reports on a novel facility designed and constructed for exposing materials with spectrally resolved UV radiation. The instrument makes it possible to investigate how the effects caused by UV radiation vary along with the wavelength of radiation. This kind of information is useful when choosing between different options of materials for a certain application in a service environment with known spectral distribution of UV radiation. Ultimately, it can be used when aiming at identifying and isolating the various reactions and processes behind an observed property change.

In Paper V, a new approach in deriving the action spectrum of degradation of a material is proposed. The approach is based on the experimental results obtained using the facility reported in Paper IV for exposing the material samples to spectrally resolved UV radiation. Post-exposure testing of the samples aged over periods of different duration is used to quantify the property change in the material, and modelled by employing a logarithmic formula. The resulting action spectrum may be used in optimizing the chemical and/or physical protection of the material against UV radiation.

2 Materials and methods

2.1 Ultraviolet (UV) radiation

Ultraviolet radiation is electro-magnetic radiation comprising of photons with wavelengths covering the range from 10 nm to 400 nm. The natural source for UV radiation is the Sun. In the solar spectrum, the band of UV radiation is positioned between the visible radiation (400 nm – 700 nm) and X-rays (0.01 nm – 10 nm). Artificial sources of UV radiation include various lamps with emission spectra covering the UV wavelengths.

The limits between the different UV bands are based on conventions. No sharp physical boundaries between the bands hence exist, and the upper limit of the UV band, for instance, overlaps with the lower limit of the visible range. Visible radiation with the shortest wavelengths is perceived as violet in colour by the human eye. This has given the impetus to name the wavelength range underneath as ultraviolet (ultra (lat.) = beyond).

The energy of a photon is inversely proportional to its wavelength. Energies encountered in UV radiation are hence higher than those of visible radiation but lower than those of X-rays. In practice, they are high enough to induce effects that cannot be induced by visible radiation in interaction with the substance.

2.1.1 Occurrence of UV radiation

2.1.1.1 Solar UV radiation at the Earth's surface

The origin of solar radiation is in the energy released by the nuclear reactions in the interior of the Sun. From the interior, the energy propagates outward by radiation, convection, and conduction to the photosphere of the Sun. From the photosphere, energy is emitted as electromagnetic radiation with continuous spectral distribution corresponding to a thermal source with an effective temperature of approximately 5800 K. Atomic absorption processes occurring in the layers above the photosphere, the chromosphere and the corona, superimpose the characteristic Fraunhofer lines onto the solar spectrum (Liou, 2002).

More than 90 % of the radiant intensity in the solar spectrum is attributable to the visible and infrared radiation. At top of the Earth's atmosphere, the contribution of UV radiation in the solar spectrum is below 10 %. Interaction between the constituents of the atmosphere and the traversing photons involves a variety of different scattering and absorption processes. All of these processes are wavelength-specific. Hence, in a macroscopic sense, the atmosphere acts like a filter removing photons with certain wavelengths from the solar spectrum. As a result, the contribution of UV radiation in the solar spectrum at the Earth's surface is usually less than 8 % (Webb, 1998). Moreover, the UV-C band, i.e.: UV radiation with wavelengths below 280 nm, is filtered out almost completely.

There are several factors that affect the intensity of solar UV radiation at the Earth's surface. These may be grouped as follows: 1) the location of the observation site in relation to the Sun and the atmosphere; 2) the constitution of the atmosphere above and below the site; and 3) the reflective properties of the ground around or below the site.

The position of a terrestrial observation site in relation to the Sun depends on the distance between the Earth and the Sun, the time of the day, the season, and the geographical location of the site. The last three factors determine the position of the Sun in the sky. As a measure for the height, the angle between the local vertical direction and the direction of the center of the solar disk is commonly used. This parameter is called the solar zenith angle. The constitution of the atmosphere essentially covers all constituents involved in the absorption and scattering processes in the radiative transfer. The reflective properties of the ground are defined by the local topography and the state of the ground.

The annual minimum and maximum Sun-Earth distances differ by approximately 3.4 %, imposing a maximum annual difference of approximately 7 % in the intensity of extra-terrestrial radiation (Madronich, 1993). The variations in the solar zenith angle are far more significant in comparison. The diurnal variations stem from the axial rotation of the Earth, and the seasonal ones from the change in the inclination angle of the Earth orbiting around the Sun. Both types of alternation depend on the geographical location of the observation site. The daily variation, limited by the minimum and the maximum elevation of the Sun during the day, depends additionally on the season.

The transfer of UV radiation through the atmosphere is regulated by the atmospheric constituents. In addition to the nitrogen and oxygen molecules N_2 and O_2 , these include molecules of various trace gases like ozone O_3 , sulphure dioxide SO_2 , nitrogen oxide NO_2 ; water H_2O in states of gas (water vapour) as well as liquid and solid (water drops and ice crystals in clouds); and different aerosols (e.g., dust, soot, sea-salt, sulphuric acid) of both natural and anthropogenic origins. The regulative effect of these factors on UV radiation is based on the interactive processes taking place between the photons and the constituents. The amount of the different constituents in a volume element varies in time and location, horizontally as well as vertically, which results in temporal and spatial variations in the attenuating effect of the atmosphere on solar UV radiation.

The interaction between UV radiation and atmospheric constituents appears as processes of extinction. Two different mechanisms contribute to extinction: absorption and scattering. In an absorption process, the energy of the photon is transferred to internal energy of the absorbing constituent. As the photon is removed from the beam propagating through the medium, the radiative intensity of the beam is reduced. Molecular absorption can only occur if the energy of the photon is high enough to raise the molecule into an excited state. Ozone and oxygen in the upper atmosphere are the most important molecular absorbents in the UV range. Absorbance of aerosols depends on the type of the particle: sulphate aerosols and particles containing organic acids and water exhibit hardly any absorbance (Lund Myhre & Nielsen, 2004), whereas, for instance, dust and smoke do absorb in the UV range (Herman et al., 1997). For cloud droplets, only weak absorption has been found (Madronich, 1993).

For scattering, two types of processes are dominant in the atmospheric radiative transfer: Rayleigh scattering and Mie scattering. Rayleigh scattering is elastic scattering of radiation by molecular atmospheric constituents. The intensity of Rayleigh scattering is proportional to λ^{-4} . Forward and backward scattering are approximately equal. Mie scattering occurring on aerosol particles and cloud droplets has higher probability for forward scattering. As the size of the scattering particle exceeds the wavelength of the incident radiation, additional weaker maxima in other directions appear as well. To assess the effect of the particle size on scattering, a term called size parameter α may be used. For a spherical particle with radius r , the size parameter is defined as the ratio of the particle circumference to the wavelength of the incident radiation:

$$\alpha = 2\pi r / \lambda. \quad (1)$$

The magnitude of the size parameter α determines the main mechanism for scattering. For $\alpha \ll 1$, Rayleigh scattering occurs, whereas for $\alpha \approx 1$, Mie scattering can be expected (Madronich, 1993).

The probability of an absorption (scattering) process along a path of a photon is described by the absorption (scattering) cross section σ_a (σ_s). The cross section is specific to the absorbing (scattering) constituent and gives the probability of an absorption (scattering) process to occur along the path of a photon. The quantity describing the relative magnitude of absorption and scattering is called the single scattering albedo ω_0 , defined as

$$\omega_0 = \frac{\sigma_s}{\sigma_s + \sigma_a}. \quad (2)$$

For pure absorption, $\omega_0=0$, and for pure scattering, $\omega_0=1$ (Lenoble, 1993). The former is referred to as the conservative case with no loss of radiative energy. However, this limit cannot be reached in reality. The latter limit may be used as an approximate in cases where the scattering is negligible in comparison to absorption. Usually, ω_0 is strongly dependent on wavelength (Madronich, 1993).

In principle, all atmospheric constituents are capable of both absorbing and scattering radiation. However, they do differ in respect of the probability of the processes. For molecules, either one of the processes often exceeds the other, as the molecular absorption processes are confined to narrow spectral bands. For aerosol particles and cloud droplets, both processes may take place with measureable probability (Madronich, 1993).

Amongst all the constituents in the atmosphere, ozone often gains special attention. Ozone has strong absorption bands both in UV-C and UV-B region and hence significantly contributes to the UV attenuating effect of the atmosphere. Decrease in the atmospheric column ozone may be expected to increase the amount of UV radiation reaching the Earth's surface – a phenomenon already witnessed. Ever since the discovery of the ozone hole over Antarctica in 1985 (Farman et al., 1985), stratospheric ozone has been of general concern and under intense monitoring (UNEP, 1998; 2003; 2012).

The amount of scattering and absorption processes potentially encountered by radiation incident to the Earth's atmosphere does not depend solely on the composition of the atmosphere. It also depends on the solar zenith angle, which determines the thickness of the airmass traversed by radiation, i.e.: the length of the rectilinear path of the direct solar beam from the top of the atmosphere to the ground. The bigger the solar zenith angle, the thicker the airmass traversed by radiation, the more chances for the photons to interact with the atmospheric constituents, and the larger portion of the incident radiation gets attenuated.

The altitude of the observation site also has an indirect influence to the solar UV radiation at the Earth's surface. At high altitudes, the atmosphere above the site is thinner, and contains a smaller amount of attenuating constituents compared to the atmosphere above sites at lower altitudes. Hence, higher levels of UV radiation are encountered at high altitude sites than at sea level. This so called altitude effect varies from 7 % to as high as 24 % per kilometer for the UV wavelengths (Blumthaler et al., 1994; Piazena, 1996; Blumthaler et al., 1997; Alexandris et al., 1999).

Yet another factor affecting the solar UV radiation at the Earth's surface is the reflective property of the ground. The reflectance is defined as the ratio of the irradiance upwelling from the ground and the irradiance downwelling from the atmosphere. The surface acts like a boundary between two media of different refractive indices. Following the Fresnel's law, part of the radiation received by the surface is reflected back into the atmosphere. Two types of reflection processes may be distinguished: specular and diffuse. Specular reflection is mirror-like reflection into a single direction determined by the angle of the incoming radiation. In diffuse reflection, radiation is reflected into several different angles. The portion not reflected at the surface is refracted into the reflective medium. Some of the penetrated radiation may be scattered back into the atmosphere, appearing as diffuse reflection. Practically all grounds exhibit both diffuse and specular reflection. In most cases, the component of the diffuse reflection is more dominating (Lenoble, 1993).

The reflectance, commonly called albedo (lat. albus, "white"), depends on the type of the ground, the wavelength of the incident radiation, and in general the angle of incidence. Over grassland, albedos as low as approximately one percent has been measured (McKenzie et al., 1996) in UV wavelengths. Over fresh snow, albedos exceeding 90 % has been reported (e.g., Blumthaler & Ambach, 1988; Grenfell et al., 1994; Kylling et al., 2000). Strong seasonal dependences in albedo are hence encountered at locations with seasonally snow-covered grounds. The topography of the terrain may also affect the albedo by imposing shadows or merely changing the angular distribution of the radiative field on the location of observation (Madronich, 1993).

It is noteworthy that the variability of solar UV radiation at the Earth's surface includes both the spatial and temporal dimension (e.g., Zerefos et al., 1997; Udelhofen et al., 1999; Chubarova & Nezval', 2000; Herman et al., 2000; McKenzie et al., 2003; Seckmeyer et al., 2008). The temporal variations include the clearly distinguishable diurnal and annual cycles that originate from the planetary motion of the Earth. The basic shape of these cycles is similar at any location on the Earth, but the amplitude and width of the cycle vary according to the geographical location of the observation site. On these cycles are imposed the effects

caused by the atmospheric conditions and the reflective properties of the terrain, both of which also possess seasonal variability of their own. It is hence clear that the time series of UV radiation of a particular site are specific to the site and representative to that site only.

2.1.1.2 Artificial UV radiation

UV radiation may be artificially produced using a lamp with an emission spectrum overlapping with the UV radiation wavelengths. These include lamps based on a range of different technologies: gas discharge lamps, LEDs (Light Emitting Diodes) and lasers (McGreer, 2001). The radiative properties, i.e., the intensity and the spectral distribution of the radiation emitted by the lamp, depend on the technology used. Some of the lamps yield UV radiation with intensities comparable to the solar UV radiation at the Earth's surface, but also intensities far exceeding those are commonly encountered. The same applies to the spectral distribution of the radiation emitted by the lamps. The emission spectrum of a UV lamp may be continuous, or consist of certain discrete lines, either as such or as superimposed onto a continuous spectrum.

A high-pressure discharge lamp is one of the common types of artificial UV radiation sources. The lamp usually consists of a quartz bulb with electrodes, filled with high-pressurized (noble) gas and/or metal vapour. An electric discharge is produced between the electrodes of the lamp, resulting in ionization of the gas/vapour and emergence of free electrons in the plasma. Collisions between the free electrons accelerated by the electrical field and the gas/vapour atoms inside the bulb excite some electrons in the atomic orbitals to higher energy states. Return to a lower energy level produce photons with characteristic wavelengths (Koller, 1965).

Examples of high-pressure discharge lamps commonly used for exposing materials with UV radiation are mercury vapour lamps and xenon arc lamps. In mercury vapour lamps, an electric arc through vaporized mercury acts as a source of radiation. The radiative output contains characteristic spectral lines of mercury. Although partly superseded by newer metal halide lamps, mercury vapour lamps are still chosen for many applications due to their efficiency and long life time (see, e.g., Anton-Prinet et al., 1998; Liauw et al., 1999; Sthel et al., 1999; Claudé et al., 2001; Peinado et al., 2002; Sabaa & Mokhtar, 2002; Allen et al., 2004; Bussière et al., 2005; Kaczmarek et al., 2005; Shanmugharaj et al., 2005; Boersma, 2006; Rivaton et al., 2006; Grelier et al., 2007; Neumann et al., 2007). In xenon arc lamps, the arc is produced by a discharge through ionized xenon gas. The spectrum of the resulting radiation is continuous with no prominent emission lines, imitating fairly closely the spectrum of solar radiation at the Earth's surface (Searle et al., 1964).

Both the above mentioned lamps are commonly used for artificial ageing of materials. The most obvious benefit of using artificial ageing is the possibility to use intensities higher than those naturally prevailing outdoors, hence accelerating deterioration and gaining knowledge

on the ageing behaviour of the material in a shorter period of time. Another reason is the ease of regulation, monitoring and quantification of the factors contributing to the ageing.

In artificial ageing of materials, UV lamps are usually installed into a certain chamber where the material samples are placed inside for exposure. This solution provides a fixed repeatable geometry for the exposure and ensures that no UV radiation induced damages are caused to living creatures or materials that are not intended to be studied for their ageing behaviour. Furthermore, the chambers may be equipped with functions enabling weathering of materials with other ageing factors than UV radiation, like elevated temperatures and periodic water sprays (e.g., McGreer, 2001; Searle, 2003). Commercial chambers are available abundantly, but also ad-hoc built ones are used.

2.1.2 Quantification of UV radiation

The basic physical quantity in quantification of UV radiation is spectral irradiance $E_{e\lambda}$, denoting the power of electromagnetic radiation per unit wavelength and per unit area incident on a surface, in SI units $\text{Wm}^{-2}\text{nm}^{-1}$. From this basic quantity, several other quantities may be derived. Integration of this quantity over the wavelengths yields (broadband) irradiance E_e in SI units Wm^{-2} . Integration of irradiance E_e over time produces radiant exposure H_e in SI units Jm^{-2} . Temporal integration may be similarly performed on spectral irradiance $E_{e\lambda}$, to yield spectral radiant exposure $E_{e\lambda}$ in SI units $\text{Jm}^{-2}\text{nm}^{-1}$. The first three quantities are well established and widely used, whereas the fourth is more uncommon. However, it has been recognized as potentially most useful for quantification of radiative exposure on materials when investigating wavelength-dependent effects of radiation (Heikkilä et al., 2007).

In a geometrical consideration, solar UV radiation at the Earth's surface may be divided into a direct and diffuse component. The sum of the direct irradiance and diffuse irradiance make up the total irradiance, commonly called global irradiance (Madronich, 1993). The direct irradiance composes of photons received from the direction of the Sun from a solid angle determined by the solar disk. The diffuse component results from photons scattered from the solar beam in the atmosphere, or reflected from the ground back to the atmosphere. Both the photons once scattered and the photons reflected from the ground may encounter further scattering in the atmosphere. This phenomenon, called multiple scattering, may significantly enhance diffuse radiation in the UV wavelengths where Rayleigh scattering is strong. With these considerations in mind, it is clear that the distribution of UV radiation is not uniform in all directions. Instead, a certain angular distribution of radiation prevails. The quantity used for measuring radiation falling within a given solid angle (in steradians, sr) in a specified direction is spectral radiance $L_{e\lambda}$, in SI units $\text{Wm}^{-2}\text{nm}^{-1}\text{sr}^{-1}$. Spectral irradiance primarily used for the quantification of UV radiation is in fact spectral radiance integrated over the 2π solid angle seen by the receiving surface.

Solar UV radiation at the Earth's surface may be quantified by measurement, by calculation, or by combining measurements with modelling. Direct measurements are carried out employing in situ ground-based radiometers. Measurements may be also made indirectly by a radiometer onboard a satellite orbiting the Earth, yielding space-borne quantities of UV radiation. These measurements are satellite-derived since the final UV quantities are derived by computations from the measurements of radiation reflected from the Earth back into the space. Calculations involve use of radiative transfer models and knowledge on the location of the site, the position of the Sun, the state of the atmosphere and the properties of the ground. Modelling may be also used in combination with the measurements, for filling in the gaps in the measured time series of UV irradiance, for instance, or for reconstructing a time series of UV irradiance for a site or period of time for which no measurements are available.

2.1.2.1 Measurement of UV radiation

2.1.2.1.1 Ground-based in situ measurements

Three basic types of instrumentation are currently in use for ground-based in situ measurements of solar UV irradiance: spectroradiometers, broadband radiometers and multifilter radiometers (Webb, 1998; Seckmeyer et al, 2001; Seckmeyer et al., 2005; Seckmeyer et al. 2010; Aphalo et al., 2012). The instruments are mainly installed to measure UV irradiance on a horizontal surface, but other orientations such as vertical ones are used for certain purposes. Spectroradiometers measure the spectral irradiance, generally with a wavelength step of 1 nm. Broadband meters measure the irradiance integrated over a certain wavelength band, such as UV-B. Multifilter radiometers measure irradiance integrated over a few narrow spectral bands with specified center wavelengths. In practice, the choice of instrumentation depends on the objectives of the study as well as the resources available for the maintenance. Guidelines on successful operation with exhaustive QC/QA procedures are currently available for all the main categories of instruments (Webb et al., 1998; 2003; Blumthaler, 2004).

The main principle of operation in all instruments measuring horizontal UV irradiance is the same. The instruments are equipped with foreoptics for gathering photons, a detector for measuring the energy of the received photons, and a logger to record the data. In spectroradiometers, an additional device called monochromator is employed between the foreoptics and the detector to resolve the incoming radiation into spectral components. In essence, the monochromator passes through only photons with certain wavelength to be detected at a time, while rejecting all the others. Usually the monochromator is programmed to scan over a certain wavelength range, resulting in a spectrum of irradiance. A single monochromator spectroradiometer employs only one monochromator. In double monochromator spectroradiometers, the incoming photons are guided through two consecutive monochromators. In general, double monochromators are preferred as they exhibit significantly better stray light rejection as compared to the single monochromators.

The horizontally mounted measurement head has a field-of-view of 2π steradians, meaning that it sees the whole hemisphere above and around it. The measurement head collects all the photons from all directions of the hemisphere onto a diffuser. The traditional material for the diffuser is teflon, but novel materials like ground quartz and quartz with imbedded air bubbles are also available. The diffuser is needed to eliminate the potential directional dependence in the measurement and the collection of photons in compliance with the cosine-law. The evenly diffused photons are guided to the detector to produce a measurable electric quantity proportional to the energy of the photons. As a detector, scanning spectroradiometers typically employ photomultiplier tubes, whereas in other types of instruments, a semiconductor detector is used. Recently, spectroradiometers employing array semiconductor detectors has been also developed. The advantage of the array spectroradiometers is that they measure the entire spectral region of interest at the same time (Seckmeyer et al., 2010; Aphalo, 2012).

The main difference between the different types of instruments is in their accuracy. In this respect, scanning spectroradiometers equipped with double monochromators are considered state-of-the-art instruments (Seckmeyer, 2001). Instruments also differ by the extent to which they yield knowledge on the spectral distribution of the incoming radiation. Again, in this respect, spectroradiometers are considered superior. In broadband measurements, all information on the spectral distribution is lost. With the filter radiometers, information of intermediate spectral resolution is obtained. Another important difference lies in the temporal resolution of the measurements. Scanning spectroradiometers measure the wavelengths one after the other, resulting in temporal resolution far beyond that given by the other types of instruments.

2.1.2.1.2 Space borne satellite-derived measurements

Ever since the 1970's, several meteorological satellites orbiting the Earth have been equipped with spectrometers capable of measuring extra-terrestrial and backscattered solar radiation. Backscattered radiation is radiation scattered by the Earth's atmosphere back to the space. Direct measurement of solar radiation at the Earth's surface is not possible for a space borne instrument. However, measurements of backscattered radiation can be used to infer estimates for solar radiation by employing radiative transfer calculations.

The Total Ozone Mapping Spectrometers (TOMS) instruments form one class of the spectrometers utilized for space-borne satellite-derived measurements. One of the instruments of this kind was flying onboard the Sun synchronous Earth Probe (EP) satellite of the National Aeronautics and Space Administration (NASA) during the time period of 25 Jul 1996 – 20 Jun 2004. TOMS/EP was a single monochromator spectrometer measuring the irradiance and the radiance backscattered by the Earth's atmosphere on six selected UV wavelength bands with centre nominal wavelengths of 308.6 nm, 313.5 nm, 317.5 nm, 322.3 nm, 331.2 nm, and 360.4 nm. The instrument looked at the Earth through a point in a direction perpendicular to the orbital plane. The area seen by the instrument was determined

by its Instantaneous Field of View (IFOV) of 3 degrees x 3 degrees, corresponding to an area of 26-60 km² x 26-33 km² on the Earth (Herman et al., 1999). A mirror was used to move the field of view for the scan in steps of 3 degrees. The scan ranged from 51 degrees on the left side of spacecraft nadir to 51 degrees on the right, resulting in a total of 35 samples per scan in only eight seconds (McPeters et al., 1998).

The primary product derived from the measurements performed by TOMS is the total ozone column in the Earth's atmosphere. The retrieval is done by comparing the measured normalized radiances and radiances obtained by radiative transfer calculations for different ozone amounts and the conditions of the measurement. The retrieved total ozone values may be further used for retrieval of solar UV irradiance at the Earth's surface. One of the methodologies of this kind has been developed within the establishment of the PROMOTE UV Data Archive (Tanskanen & Lindfors, 2008). The approach adopted therein employs pre-calculated multidimensional Look-Up Tables (LUTs) tabulating values for aerosol optical depth, aerosol single scattering albedo, altitude, cloud optical depth, solar zenith angle, surface albedo, and total ozone column. In creating the LUTs, the SDISORT solver included in the libRadtran radiative transfer software package (Mayer & Kylling, 2005) is used. By interpolation using the LUTs, the irradiance for a clear-sky case and the factors for the attenuation caused by aerosols and clouds are determined, of which the final product, the solar irradiance prevailing on the surface of the Earth, is calculated.

From the derived solar spectral irradiance, different data products may be further computed. Within PROMOTE, for instance, daily erythemal UV doses are calculated. The derived spectral irradiances in temporal resolution of an hour are first weighted with the action spectrum for erythema (sunburning) defined by CIE (Commission Internationale de l'Eclairage) (ISO/CIE, 1999). The CIE erythemal action spectrum describes the sensitivity of human skin to noticeable reddening. Next, the corresponding CIE erythemally weighted dose rates are calculated by integration over the wavelengths. Finally, the dose rates are integrated over the time of the day, to yield the daily erythemally weighted UV dose. This quantifies the dose accumulated in the course of the day onto a horizontally oriented surface possessing the sensitivity defined by the applied CIE erythemally weighted action spectrum.

2.1.2.2 Modeling of UV radiation

Modeling of solar UV radiation requires a computational model for performing the calculations on the attenuation of the radiation propagating through the Earth's atmosphere, knowledge on the state of the atmosphere, the reflective properties of the Earth's surface, and knowledge on the extra-terrestrial solar spectrum at top of the Earth's atmosphere.

The attenuation of parallel radiation of a single wavelength λ incident at angle θ onto a layer of vertical thickness z with absorbing constituents in number density n (in units m⁻³) is described by the Beer-Lambert law as follows:

$$\frac{E_{e\lambda}}{E_{e\lambda}^0} = e^{-\tau(\lambda,z)/\cos\theta} = e^{-\sigma(\lambda)N/\cos\theta} . \quad (3)$$

Here, $E_{e\lambda}$ is the transmitted irradiance, $E_{e\lambda}^0$ is the incident irradiance, τ is the vertical optical depth of the constituent for absorption, σ is the absorption cross section of the constituent, and

$$N = \int ndz \quad (4)$$

is the vertical column density of the absorbing constituents (in units m^{-2}) (Madronich, 1993). In the presence of several different absorbing constituents, the total vertical optical depth is formed as a sum of the optical depths of the single constituents. The law is strictly valid for monochromatic (single wavelength) radiation, reasonably low concentrations (< 0.01 M) of absorbing constituents, and incident radiation with energy not capable of influencing the constituents (Bohren & Clothiaux, 2006).

The attenuation of monochromatic radiation by scattering may be described by the Beer-Lambert law as well by replacing the absorption cross sections of the constituents with the scattering cross sections. However, photons scattered out of the beam incident to the Earth's atmosphere create a field of radiance where photons are propagating in every possible direction simultaneously as diffuse radiation. Consequently, an approach capable of handling the attenuation of both components of solar irradiance, direct and diffuse, is needed. For this purpose, different kinds of radiative models are used.

All modeling of UV radiation is more or less based on the general radiative transfer equation. In its integrodifferential form, the equation may be expressed as follows (Madronich, 1993):

$$\begin{aligned} \cos\theta \frac{dL(\tau, \theta, \varphi)}{d\tau} = & -L(\tau, \theta, \varphi) + \frac{\omega_0}{4\pi} E_\infty e^{-\frac{\tau}{\cos\theta_0}} P(\theta, \varphi; \theta_0, \varphi_0) \\ & + \frac{\omega_0}{4\pi} \int_0^{2\pi} \int_{-1}^1 L(\tau, \theta', \varphi') P(\theta, \varphi; \theta', \varphi') d\cos\theta' d\varphi' . \end{aligned} \quad (5)$$

Here, θ and φ are the zenith and azimuth angles defining the specific sky direction from the point of observation, and θ_0 and φ_0 are the corresponding angles for the direct beam; E_∞ is the extra-terrestrial irradiance; $P(\theta, \varphi, \theta', \varphi')$ is the scattering phase function, defined as the probability for a photon incoming from the direction defined by angles θ' and φ' to scatter into the direction defined by the angles θ and φ ; and ω_0 is the single scattering albedo (Madronich, 1993). The term on the left-hand side represents the vertical change in radiance. On the right-hand side, the first term represents the attenuation due to both absorption and scattering, the second the increase of diffuse radiation resulting from the scattering of the direct beam, and the third the increase of diffuse radiation originating from scattering from other parts of the radiance field than the direct beam.

The models used for computing solar UV radiation at the Earth's surface may be categorized according to how the radiative transfer in general is treated in them. In simple parameterized models, the diffuse radiation is parameterized to represent a range of different conditions. These models are based on fitting the results of a more accurate radiative transfer with simple analytical functions (e.g., Green et al., 1980; Gueymard, 1995). These models treat the atmosphere merely as an entity, not on the level of the single constituents. The physical models, in contrast, employ the radiative transfer equation as such, and treat the interactions

between the photons and the atmospheric constituents by solving the equation. The equation cannot be solved analytically in its general form. However, several numerical methods have been developed to solve the equation. The most common techniques for numerical solving employed are discrete ordinate methods (e.g., Stamnes et al., 1988) and Monte Carlo method (e.g., Cahalan, 2005). A third category of models are based on so-called two-stream approximation (e.g., Kylling et al., 1995). These models use the radiative transfer equation in an approximate form where radiation is divided into down-welling and up-welling components (Madronich, 1993).

2.2 UV radiation and materials

Ultraviolet radiation encountering the surface of a material experiences the same interactive phenomena as when propagating through the atmosphere. The constituents on the surface of a material may either scatter or absorb the UV photons. Those photons that are not immediately absorbed by the constituents on the outer layers of the material are scattered. The photons scattered back into the atmosphere constitute to the reflected part of the incident radiation, whereas those scattered into the material make up the penetrating part. The photons penetrating into the material experience further scattering and absorption phenomena. Some of the interactions taking place on the surface of the material may lead to changes in the properties of the material. Some of the changes remain superficial, whereas the others may progress into the deeper layers and even into the bulk of the material. Most metals and ceramics are known to exhibit excellent UV durability. Polymeric materials, in contrast, are often more or less affected, despite the fact that the penetration depth of the UV photons is found for most polymeric materials to be only of the order of 50-100 microns (Chin, 2001).

The effects of UV radiation may be investigated by exposing material samples to UV radiation and by making observations on the property changes the exposure has caused in the materials. As a source of radiation, both the Sun and different types of artificial sources are used. For the material, the source of radiation is insignificant. The same kinds of changes take place under the bombardment of photons from the Sun and from an artificial source – provided that the amount per unit time and the energy distribution of the single photons in the exposing radiation is the same. This is in fact the issue that makes the testing of UV durability of materials challenging. Creating UV exposure conditions with exactly the same kind of characteristics in an experiment compared to those used in a previous experiment may be realized by employing the very same laboratory facility. With different facilities, however, this can be hardly realized. Natural outdoor climates are even more difficult to be replicated by laboratory equipment.

Observations on the property changes of materials may be quantified by suitable techniques. For proper post-exposure analysis of the changes, quantification is a prerequisite. Two basic types of measurements are adopted: non-destructive and destructive testing. Samples submitted to non-destructive testing remain in principle in their original shape. These methods include, e.g., measurements of colour, gloss, hardness, roughness of surface, and

spectroscopic methods such as UV/VIS and IR spectrometry, used in searching for changes in the molecular composition of the material. Destructive techniques include, e.g., tests for bending, tensile and impact strength. Sometimes results obtained by application of a non-destructive method may predict a change in the mechanical properties of a material. For instance, colour changes may indicate structural changes in the bulk of the material.

2.2.1 Effects of UV radiation on materials

The effects of ultraviolet radiation on materials become apparent through changes in the properties of the materials. Their colour may change by yellowing, bleaching or darkening. They may lose their gloss or transparency. Their surface may show chalking, fine cracking, or even severe erosion. UV radiation can also harden the surface of a material. Superficial changes often make way to actual structural changes in the bulk of the material. The materials may become brittle, cracked, and friable. The changes are irreversible (Searle, 2003). As a consequence, the materials lose permanently their original mechanical properties in terms of tensile, flexural, and/or impact strength, potentially leading to an untimely end of the service life time of the product. The phenomenon is very mundane but not completely harmless. In the post-modern infrastructure even the structural and semi-structural elements used in buildings, transportation etc., contain parts made of polymers potentially susceptible to UV radiation induced damages. Unforeseen deterioration in these parts may have severe consequences (e.g., Andradý et al., 1998; Karbhari et al., 2001).

The basic phenomenon deep down in the observed deterioration of materials is called photodegradation. Photodegradation is initiated by a photophysical process where the polymer macromolecule is activated through absorption of a photon of incident UV radiation. The dissipation of the excited state may lead to one of the two competing processes of photodegradation: chain scission or crosslinking. In chain scission, the backbone of the polymer breaks, resulting in formation of two molecules of lower molecular weight. In crosslinking, small groups of two neighbouring molecules link together by forming a cross-link, a covalent or ionic bond, from which consequently at least four molecular chains emanate.

A rule known as the Grothus-Draper law states that if light is to initiate photodegradation, it has to be absorbed by a molecule of the substance. Most pure polymers only contain bonds that are not expected to absorb radiation at wavelengths of UV radiation. However, practically all polymers contain at least small amounts of impurities with so called chromophoric groups which do absorb radiation at wavelengths of UV. This is the reason why photodegradation of polymers occur even when the wavelengths of the exposing radiation are longer than 300 nm.

The relationship between the number of photons absorbed and the number of polymer molecules scissioned per unit time is quantified by the quantum yield of chain scission ϕ_s as follows:

$$\phi_s = \frac{\text{Number of molecules undergoing scission reaction}}{\text{Number of quanta absorbed by the polymer}} \quad (6)$$

Respectively, the quantitative relationship between the absorption rate of photons and the number of polymer molecules involved in crosslinking per unit time is given by the quantum yield of crosslinking ϕ_c :

$$\phi_c = \frac{\text{Number of molecules undergoing crosslinking reaction}}{\text{Number of quanta absorbed by the polymer}} \quad (7)$$

Wavelength specific experimental values for quantum yields have been determined for many polymers (Rabek, 1995).

The competition between the two principal mechanisms of photodegradation may be illustrated by considering the resulting changes in the molecular weights \bar{M}_w and \bar{M}_n and molecular weight distribution \bar{M}_w/\bar{M}_n . The number average molecular weight \bar{M}_n is the statistical average molecular weight of all the polymer chains in the sample, defined as:

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i} \quad (8)$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. \bar{M}_w is the weight average molecular weight defined as follows:

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \quad (9)$$

Three main categories of photodegradation may be distinguished, characterized by different ranges of values for \bar{M}_w , \bar{M}_n , and \bar{M}_w/\bar{M}_n : absence of crosslinking (only chain scission occurring), absence of chain scission (only crosslinking occurring), and simultaneous chain scission and crosslinking reactions (Rabek, 1995).

Pure photodegradation can only take place in an inert atmosphere. The presence of oxygen complicates the scene, and instead of pure photodegradation, photo-oxidative degradation occurs. In general, photo-oxidative degradation proceeds as follows: In the initiation phase, free polymer radicals are formed. In the propagation phase, the radicals react with oxygen, producing polymer oxy- and peroxy-radicals as well as secondary polymer radicals, resulting in chain scission. In the termination phase, different species of free radicals interact with each other, resulting in crosslinking (Rabek, 1995).

In addition to oxygen, a factor that is in practice most often present in the weathering of a material is heat. The presence of heat further complicates the scene of photo-physical processes and photo-chemical reactions involved in photo-oxidative degradation. Photodegradation and thermal degradation occur simultaneously and often accelerate each other. In the actual photoageing of materials, oxygen and heat are further accompanied by many other environmental stress agents. These factors include organic solvents and mechanical stresses. For outdoor materials, water, pollutants and bio-substances like pollen, fungi and mould, are also significant weathering agents (e.g., Searle, 2003). The interactive effect of the different stress factors is often synergistic, meaning that several factors affecting

simultaneously on a material make a more severe damage than could be predicted as a net result of the effects caused by the single factors separately (Rabek, 1995).

As the photodegradation of a material can only result from photons absorbed by the molecules of the material, and the material can only absorb radiation of certain energy, the deteriorating effect of UV radiation strongly depends on its wavelength (Andrady, 1997). Certain wavelengths cause most of the damage, whereas the others do not play a role. The wavelength sensitivity of a material to a specific damage, e.g., yellowing, may be described by a material-specific spectral response. Two basic forms for the spectral response exist: an activation spectrum and an action spectrum (Trubiroha, 1989; Searle 2000). The activation spectrum has been derived for a specific light-source, limiting its use into exposures to that particular source only. The action spectrum, in contrast, has been derived in a way that accounts for the radiant exposure used in the experiment, making it more universal than the activation spectrum.

Materials may be protected against the deteriorating effects of UV radiation by imbedding suitable light stabilizers into the bulk of the material, or by applying a suitable coating or painting onto the surface of the final product (Andrady et al., 2011). Light stabilizers include various UV absorbers and free-radical scavengers. Coatings and paintings are often themselves polymers that only exhibit better durability against UV radiation than the material they cover. Their service life times are nevertheless limited by the very same processes of photoageing as those of the other polymeric materials.

2.2.2 Weathering of materials

Investigations on the effects of UV radiation on materials generally follow a two-phase procedure (Searle, 2003). In the first phase, called weathering, samples of materials are exposed to UV radiation. The weathering experiment may be conducted in natural outdoor or laboratory conditions (Masters & Bond, 1999). In an outdoor experiment, solar radiation may be used as such as a source of UV radiation. Alternatively, it may be enhanced using specific solar concentrators, making the test as an accelerated outdoor weathering experiment (Chin, 2001; Searle 2003). In experiments conducted in the laboratory, artificial sources of UV radiation are used. The intensities of UV lamps usually exceed those of solar UV radiation at the Earth's surface. As a consequence, weathering is highly accelerated. The second phase following the actual weathering includes the investigation of the weathered samples for the property changes and the analysis of the relationship between the conditions prevailing during the weathering and the quantified changes in the material properties.

The most crucial issues in all weathering tests, all the way from the planning phase to the post-exposure tests, are essentially related to the quantification of two things: the weathering agents, and the property changes caused by the weathering. With an emphasis on these

dimensions, the methods used in weathering tests in general and in the research of UV radiation effects on materials in particular are described in the following sections.

2.2.2.1 Natural weathering

Natural outdoor weathering of materials is a traditional method in testing the durability of materials intended for outdoor use. Specimens made of the material under study are installed at the mercy of the weather onto a weathering platform on a selected test site. In the choice of the site, various criteria may be used. In the United States, two sites, Phoenix in Arizona and Miami in Florida, provide weathering in environments with standardized climatological specifications (see, e.g., Searle 2003; Pickett & Gardner, 2005). The conditions at these sites are also harsh enough for the tests, exceeding those encountered by the materials in most of their normal service environments. Sometimes a network of selected sites covering a range of different climates may be considered a better solution than just one site. In all cases, the availability of data on the weathering agents is a crucial criterion for the selection of the site (Masters & Bond, 1999).

The data characterizing the weathering circumstances should cover the factors initiating and maintaining photo-oxidative and thermal degradation of materials. In addition, it is useful to have knowledge on the environmental agents contributing either through chemical reactions or physical processes to the overall ageing of materials. Heat acts as the initiator for the thermal degradation of polymers. Therefore, on-site temperature data is required. UV radiation initiates photo-oxidative degradation. Consequently, data on UV radiation exposing the materials during the weathering experiment is needed. Moisture is involved in degradation reactions either as a catalyst or a substance diluting and rinsing off the reaction products. In composite materials, absorbed water may also cause detachment of one material from another. In addition, rain water may have an abrasive effect on the surface of the materials. Data on humidity and precipitation are hence important. Any additional knowledge on other environmental factors like the quality of the air is of value (Wypych & Faulkner 1999; Searle 2003).

The weathering experiments are usually planned to follow a timetable with predefined exposure periods (Jacques, 2000). Typically, the experiment is initiated by installing a series of specimens all at the same time. The samples are removed from exposure one at a time after the elapse of the predefined time period. The length of the exposure periods may be defined as multiples of the first period, either as full years or quarters. If the first weathering period is three months, the first sample is withdrawn from exposure after three months from the initiation of the experiment, the next sample after six months etc. The initiation of the weathering test often takes place in spring, guaranteed to cause the maximum heat and UV radiation stress already on the first exposure batch.

2.2.2.2 Artificial weathering

Artificial weathering of materials is being widely used for testing the durability of outdoor materials in laboratory environment. In this approach, artificial sources are used for generating the agents weathering the materials: lamps emitting UV radiation, heaters producing heat, ozonators to generate ozone, and sprayers spraying water and other liquids. Circumstances in the artificial weathering experiments are controllable and reproducible. They allow running test series by varying only one factor at a time, enabling investigations on a wider range of combinations that could be realized in any natural outdoor weathering experiment. The laboratory environment also allows increasing the harshness of the weathering, resulting in accelerated weathering. Acceleration yields knowledge on the ageing behaviour of the material within much shorter time frames (Feller, 1995).

The equipment used in artificial weathering is manifold. It includes weather chambers designed to simulate natural outdoor conditions as closely as possible, as well as chambers constructed to accelerate photo-degradation as far as plausible (McGreer, 2001). For studies focusing on weathering caused by UV radiation, the most crucial component of the equipment is the source of radiation. The choice of the source depends on the desired weathering effect. The shape of the UV spectrum emitted by xenon lamps follows quite closely to that of solar UV radiation at the Earth's surface. The intensity of radiation is also comparable to natural outdoor circumstances in many weather chambers employing xenon arc lamps (Searle et al., 1964). Consequently, reactions and processes occurring in weathering experiments using this kind of equipment may be assumed to take place also in the service environments of the materials. However, lamps emitting radiation with intensities or spectral distribution significantly deviating from those found in the solar radiation at the Earth's surface are also used, especially when accelerated ageing is pursued. Use of lamps of this type calls for careful consideration as it may result in degradation mechanisms different from those occurring in the natural service environments of the material (Searle, 2003).

Knowledge on the radiative characteristics of the radiation exposing the materials is a prerequisite for reliable post-exposure analysis of the property changes caused by weathering. The technical specifications given by the manufacturers of the commercial chambers are rarely detailed enough, especially as regards the spectral distribution of radiation. In these cases, the weathering experiment should be always supplemented by characteristic measurements of the radiation exposing the material samples. The lamps also exhibit changes in their radiative output as they age. In addition to fading intensities, changes in the spectral shape of the irradiance are found. Without characterizing measurements, temporal changes in the irradiance remain undetected, leading to increased errors in the estimates of the exposure and, at the worst, erroneous conclusions concerning the durability of the materials.

2.2.2.3 Quantification of changes in material properties

Changes in the properties of weathered materials range from superficial changes to changes in the bulk of the material. Consequently, quantification of the changes also covers a wide range of experimental methods and instruments. The methods may be divided into two main classes. Non-destructive methods employ means that do not cause damage to the object. Destructive tests, in contrast, are usually carried out to the specimen's failure, meaning in practice the destruction of the object. The choice of the method depends on the property of interest. For the changes occurring on the surface of the specimen, non-destructive methods often suffice. In order to test the structural performance of the specimen, destructive methods may be necessary (Brown, 1999).

Colour and gloss are probably the properties most often examined on the surface of the weathered materials. Specific colorimeters and glossmeters are used for this purpose. Another properties of interest might be surface hardness and roughness. Properties most interesting in the bulk of the material are related to both strength and ductility, required to be in a certain balance in a serviceable product made of a polymeric material. In these tests, tensile/impact/flexural strength are often under examination. Dynamic mechanical analysis (DMA) is also commonly used for studying the viscoelastic behavior of polymers. Differential scanning calorimetry (DSC) can be used for examining if there are any changes in the melting point or glass transition temperature of the material. Fourier transform infrared (FTIR) (see, e.g., Andrady, 1996) and Ultraviolet–visible (UV/Vis) spectroscopy, as well as X-ray spectroscopy, are employed when studying the changes on the level of molecular constituents.

Amongst all the properties, colour may perhaps serve as the most versatile one when attempting to monitor the ageing of the material. Colour change in itself is an indication of superficial photo-degradative processes (e.g. Andrady et al., 1990; 1991; 1992). As such, it may be even used as a sufficient esthetic justification for the withdrawal of the product from its service. Moreover, colour change may also indicate structural changes in the outermost layers of the material. This means that the use of the product might have become uncomfortable or the product has actually lost some of its original functionality. Deteriorated surface, incapable of protecting the product anymore, provides an easy access for the different weathering agents into the deeper layers of the material. Degradation, once started from the surface layers, continues by propagation into the bulk of the product, potentially leading to severe changes in its mechanical properties. Change in the surface colour may hence signal something fundamental about the condition of the product.

The basis for the quantification of colour lies in the human colour perception. Three kinds of cone cells exist in the human eye, each possessing certain spectral sensitivity. These cells determine how colours are perceived in conditions with medium and high brightness. It is the levels of stimuli in these three types of cone cells that produce the sensation of colour (Hanson 2012). An objective measure for the colour may be derived by weighting the spectrum of the light by the spectral sensitivities of the cone cells, resulting in three stimulus

values fully specifying the colour. For mapping the physically produced colors to an objective description of color sensations registered in the eye, several different colour spaces have been defined. One of the most commonly used is the CIE XYZ colour space created in 1931 (CIE, 1932) still serving as a standard reference against which many other color spaces are defined.

From the tristimulus values quantifying the human colour vision, various indices suitable for follow-up of a colour changes of certain types may be derived. One of these is the yellowness index YI defined as (ASTM D1925–70)

$$YI = [1.28X - 1.06Z]/Y] \times 100, \quad (10)$$

where X , Y and Z are the tristimulus values for the colour sensation. The yellowness index is particularly sensitive for the colour perceived as yellow by human eye, being insensitive for the other colours. Indeed, the whole range of the index is occupied by different stages of yellowness. This makes it an efficient tool for the quantification of colour changes in objects that are expected to mainly undergo yellowing (e.g., Cho et al., 2003).

3 Results and discussion

In the following sections, the results of the original papers of this thesis are summarized in the order of the appearance of the studies. Section 3.1 deals with Paper I related to natural outdoor weathering in presenting a method to adjust the timing of weathering to seasonal variations in UV radiation exposure. Section 3.2 on Paper II presents the work done on the method for reconstruction of spectral UV irradiance. Section 3.3 summarizing the results of Paper III describes the method developed for characterization of UV radiation conditions in artificial weathering. Section 3.4 presenting the Paper IV deals with the facility designed and constructed for ageing material samples with narrow-band UV radiation. Section 3.5 describing the study reported in Paper V focuses on the method suggested for derivation of an action spectrum of photoyellowing.

3.1 Adjusting weathering periods to annual cycles of UV irradiance

The lengths of the weathering periods are typically defined using fixed durations, like multiples of a month or three months (Jacques, 2000). Ideally, material samples in an experiment of natural outdoor weathering would receive well-defined exposures of UV radiation over the weathering periods. Unfortunately, for periods of fixed duration, this is not the case, as solar UV radiation at the Earth's surface exhibits natural cyclic variability in time, always accompanied by temporal variations caused by local atmospheric and environmental factors. Consequently, UV exposure accumulated at a specific site on a material sample over three winter months may substantially differ from that accumulated over three summer months.

One approach in overcoming the problems related to the outdoor UV exposures over fixed time periods has suggested restricting the final analysis of samples to a subset least affected by seasonal variations in UV radiation, including, for instance, only samples weathered for 0, 12, 24, 36 months etc. (Klemann, 2003). This solution may exclude a substantial amount of samples from the analysis. Another solution proposed would use a certain shift factor in the post-exposure analysis as superimposed onto the abscissa of exposure times (Pickett & Gardner, 2005). For exposure durations less than a year, this approach has been nevertheless found ineffective.

In this study, a method based on prior knowledge on the local seasonal cycle of UV radiation was developed to adjust the durations of the weathering periods to the local UV radiation conditions. The study uses the daily erythemally weighted UV doses derived from the measurements performed by the Total Ozone Mapping Spectrometer (TOMS) instrument onboard NASA's Earth Probe satellite over the time period of 25 Jul 1996 – 20 Jun 2004. The reasons for the choice of data were in their free availability and erythemal weighing with an emphasis on UVB wavelengths where many materials are known to undergo photodegradation. Periods with fixed durations of 1, 3, 7, and 14 months (30, 91, 213, and

426 days) were used as starting points in the adjustment as required by an industrial partner of the project.

The selected UV radiation data was used to derive a prediction of UV exposure accumulation starting from a known date of launch for the weathering experiment. Predictions were calculated for seven European sites included in the experiment: Sodankylä, Jokioinen, Lindenberg, Ispra, Thessaloniki, El Arenosillo (Lisbon), and Izaña. For each site, a climatological annual cycle of daily UV dose and the annual average of the daily UV dose were first calculated. Next, the time series for the daily cumulative UV dose were computed. From the time series, the date with cumulative UV dose reaching 1/12, 3/12, 7/12 and 14/12 of the total annual UV dose was searched. Finally, the length of the adjusted time period of exposure was derived by subtracting the test initiation date from the dates determined in the previous step.

The effect of the adjustment was evaluated in terms of the change in the predicted accumulation of UV dose over the weathering periods. The relative change was found to range from 5 to 82 %, being most significant for the period with an original duration of 3 months. In addition, the adjustment proved increasingly important towards higher latitudes. The period least sensitive to adjustment was the 426-day-period dominated by the full annual cycle. All adjustments were found to result in extensions of the original time periods since the test was initiated in the autumn when the cycle of daily UV dose declines in the northern hemisphere.

The method developed is not confined to any particular test initiation dates or duration of exposure periods. Indeed, the adjustment described is applicable to weathering tests conducted at any location according to any timetable. The only prerequisite is an estimate on the annual cycle of the daily UV exposure. This estimate may be inferred from ground-based or space-born measurements, or radiative transfer simulations. Application of the method enhances reproducibility of the weathering tests conducted in natural outdoor conditions. In addition, it simplifies the comparison of the property changes observed in consecutive batches of samples.

3.2 Reconstruction of solar UV irradiance at the Earth's surface

Analysis of the property changes quantified in material samples weathered outdoors require knowledge on the magnitude of the environmental stress agents, including UV radiation, responsible for the changes. Ideally, quantification of UV exposure is based on simultaneous, perfectly continuous in situ measurements of spectral UV irradiance. In practice, this is often a requirement that cannot be completely met. Programmes of spectral UV irradiance measurements employing state-of-the-art spectroradiometers with their exhaustive QC/QA procedures require extensive resources (see, e.g., Seckmeyer et al., 2001; Lakkala et al., 2008), and even when such measurements are conducted, the final data sets always contain days with missing or insufficient amount of single measurements.

Determination of the total exposure having contributed to the ageing of the samples over the whole weathering test requires complete data sets with daily values for each and every day. Data for the missing days have to be somehow estimated and imputed into the original data set. The estimation may be based on, for instance, long-term climatology or interpolation between consecutive days. Uncertainties of estimated imputed daily values are larger than those truly measured. Increase of missing days hence increase the overall uncertainty of the cumulative UV quantities computed from the time series. In addition, as the effects of the UV radiation depend on wavelength, spectrally resolved measurements are often preferred. There is therefore a strong need for a method to fill in the gaps caused by the missing data in the time series of measured UV irradiance. Techniques for reconstruction of UV irradiance have been presented, making use of pyranometer measurements of global radiation over the wavelength range of 300 – 3000 nm (e.g. Fioletov et al., 2001; Feister et al., 2002; den Outer et al., 2005; Lindfors et al., 2007). However, the former efforts were focused on exposures weighted by a particular action spectrum or on specific wavelengths only.

In this study, a reconstruction method to yield spectral UV irradiance was developed. The method employs the freely available and extensively tested libRadtran radiative transfer modelling package (Mayer & Kylling, 2005; Mayer et al., 1997). Daily UV exposures were simulated for two Finnish sites, Jokioinen and Sodankylä, for which input data required by the model were available from the observatories maintained by the Finnish Meteorological Institute. The solver named sdisort, based on the discrete ordinate method and application of a pseudo-spherical correction for large solar zenith angles (Dahlback & Stamnes, 1991), was used in simulations. Pyranometer measurements of global radiation were used to infer an estimate how the cloud cover attenuates radiation on the wavelengths of UV radiation. This was realized by constructing a look-up-table for the cloud optical depth τ at wavelength of 550 nm (τ_{550}) through radiative transfer simulations of global radiation. The resulting look-up-table yielded the cloud optical depth τ_{550} as a function of measured global radiation, solar zenith angle, global albedo, and total water vapour column. Over the wavelengths of UV radiation, a parameterization based on the cloud optical depth at 550 nm, as given by the look-up-table, was derived and used in actual simulations of solar UV irradiance.

In addition to the cloud optical depth, total ozone column, total water vapour column, surface albedo, and the geographical location (latitude, longitude and altitude) of the site were used as inputs to the model in simulations of solar UV irradiance. The winter time surface UV albedo was estimated from the measurements of snow depth, with typical values of 0.4 and 0.6 for Jokioinen and Sodankylä, respectively (Arola et al., 2003). For the snow-free periods, constant value of 0.05 was used for both sites.

The method was validated against in situ ground-based measurements performed by the spectroradiometers in Jokioinen and Sodankylä. As a quantity in this study, daily spectral UV exposure computed from the simulated and measured spectra were used. This is the quantity most relevant in quantifying the exposure accumulated onto material samples aged in an outdoor weathering experiment. Estimation on the performance of the method was mainly based on two statistical numbers: the root-mean-square (RMS) of the relative difference, and the mean relative difference. The former was perceived representing a measure of the

dispersion in the difference between the reconstructed and the measured exposure. The latter, on the other hand, was considered representing the systematic deviation in the difference between those two.

The daily spectral UV exposures computed from the reconstructed hourly UV irradiances were compared against those calculated from the spectra measured by the spectroradiometers at Jokioinen and Sodankylä over the years 1995-2006 and 1990-2006, respectively. The comparison was restricted to the wavelength ranges with the upper limits defined by the upper limit of the scanning range of the instruments, i.e., 365 nm for Jokioinen and 325 nm for Sodankylä. The lower limit was set to 300 nm as a consequence of the requirement set for the minimum number of daily scans considered sufficient to yield a reliable estimate on the daily accumulation of UV exposure.

The correlation between the reconstructed and measured daily exposures was found to be very good, being in general above 0.99. More importantly, the mean percentage difference was found mostly within ± 8 %. In addition, the RMS difference was found around 10 % for wavelengths longer than 310 nm and for days with daily minimum of solar zenith angle of 70 degrees. Both the RMS and the mean difference may be compared with the total uncertainty of the measurements, estimated being approximately 10 %. In this respect, good performance of the method could be concluded.

The increase in the RMS difference towards shorter wavelengths could be attributed to the generally known increase in uncertainties in both measurements and modelling of the shortest wavelengths of solar UV radiation. For the systematic deviation, uncertainties related to the inputs for surface albedo and aerosol optical depth could be identified as the most plausible explanation. More pronounced differences on a few individual wavelengths could be seen as differences in the manifestation of the fine structure of the solar spectrum as measured by a ground-based spectroradiometer with a certain slit function and simulated by a model employing an extra-terrestrial spectrum derived from space-born measurements with an instrument with a different slit function.

The validation of the method developed for the reconstruction of solar UV exposure proved the method suitable for completing the measured time series of UV irradiance data sets. As a result, reliable estimates on the UV exposure accumulated onto material samples can be derived. For weathering experiments with no on-site measurements of UV radiation, the method could even provide a means to derive the whole data set required for the estimation of the exposure, if only knowledge on the local atmospheric and environmental factors, required as inputs to the model, are available.

3.3 Characterization of UV radiation conditions in artificial weathering

Artificial ageing is widely used in material testing. This is because weathering conducted in laboratory may be significantly accelerated by an appropriate choice of radiative source.

Hence, materials may be expected to exhibit property changes in significantly shorter time periods in an artificial than in a natural outdoor weathering experiment.

Quantification of UV exposure in artificial ageing has to be approached from a different direction than in outdoor weathering. Continuous in situ spectral measurements are often preferred in natural weathering experiments, yielding a truthful estimate on the UV exposure accumulated onto the material samples. Artificial ageing, in contrast, seldom employs online measurements of UV radiation. The dimensions of the ageing chambers simply do not allow placing a measurement head of a spectroradiometer inside. In addition, the intensity levels of UV radiation might be high enough to cause the teflon diffuser of the measurement head to deteriorate. Instead of continuous online measurements, the radiative conditions prevailing in the ageing chamber should be measured before starting exposing a batch of samples – ideally also after ending the exposure. These kinds of measurements may be called characterization of the UV radiation conditions in artificial weathering.

Previous reports on methods for characterization of UV radiation conditions in artificial ageing environments are practically not available in public. It is most probable that methods have been developed but they have remained confidential, possibly due to the competitive advantage they have provided. However, comparisons between the natural outdoor weathering circumstances and accelerated ageing environments have no grounds whatsoever without knowledge on the true exposure on the artificially aged material samples. Therefore, there is a need for dissemination of procedures and practices found applicable and useful in settling the radiative properties of the equipment used in artificial ageing of materials.

This study reports on a methodology developed for characterizing a chamber used for artificial ageing of materials for its UV radiation conditions. The method is based on measurements of spectral UV irradiance inside the chamber, carried out with a spectroradiometer, and a geometrical analysis on the radiative field measured by a broadband radiometer. The measurements were used to derive the effective exposure expected to accumulate onto the samples placed inside the chamber for ageing. Moreover, the UV conditions in the chamber were linked to those prevailing outdoors under the Sun.

The characterized UV chamber was equipped with four 300-W Ultra-Vitalux mercury vapour lamps from Osram arranged in a square formation and installed on the ceiling of the chamber. Measurements of spectral UV irradiance produced by the lamps were carried out by placing a measurement head of a Bentham DM150 double monochromator spectroradiometer on the round sample plate on the bottom of the chamber. The measurements were repeated twice: for new lamps and for lamps used for over 4000 hours.

For deriving an estimate for the effective exposure onto the material samples, measurements on the shape of the radiative field created by radiation emitted by a single mercury vapour lamp were utilized. The measurements had been carried out in a previous study using a broadband Solarmeter 6.2 with spectral sensitivity weighing the UVB wavelengths (Baines 2007). Knowledge on the geometrical distribution of UV radiation emitted by one lamp was used to compute the exposure at different locations on the sample plane, emerging as a joint

field created by the outputs of the four lamps. The computed planar exposure field was further used to derive an effective exposure onto samples of size 12.5 cm x 12.5 cm placed on the perimeter of the rotating sample plate.

In the final step of the analysis, the derived artificial effective UV exposure was compared to the natural UV exposure defined by the spectral UV irradiance measurements conducted in Jokioinen, Finland. Acceleration factors computed on the basis of the exposure levels were used to establish a link between the accelerated and natural ageing conditions.

The measured spectra showed distinct peaks corresponding to the emission lines of mercury. Comparison between the irradiances measured for new and old lamps revealed substantial fading in the intensity of the lamps. Furthermore, the fading was found to strongly depend on wavelength, being most pronounced at the shortest wavelengths of UV radiation. In the derived sample plane exposure, significant radial dependence was found. Over two-fold exposures prevailed directly beneath the single lamps compared to that prevailing in the center of the sample plate.

It could be concluded that the exposure onto the samples notably depended on the age of the lamps, on the position of the samples on the plate, and on the wavelength range considered. As a consequence, the acceleration factors computed to establish a correlation between the artificial and natural ageing conditions were also wavelength dependent. In addition, the spectral distribution of the exposure notably differed from that of the natural solar radiation at the Earth's surface, with distinct peaks at certain wavelengths. The findings are of paramount importance in estimating the relevance and transferability of the results obtained by artificial ageing to the real service environments of the material.

The presented methods are not confined to any particular equipment used for artificial ageing of materials. On the contrary, they can be employed in characterization of any instrument with a volume large enough for a measurement head of a spectroradiometer to be placed inside.

3.4 Facility for exposing materials with narrow-band UV radiation

The deteriorating effect of UV radiation strongly depends on the wavelength of the radiation. In addition, the spectral sensitivity of each material is unique and specific to that particular material (Andrady, 1997). In weathering experiments, knowledge on the spectral distribution of the exposing UV radiation is required for reliable estimation on the UV exposure accumulated onto the material samples over the weathering periods. In the post-exposure analysis of the property changes, however, this knowledge alone does not suffice. Indeed, knowledge on the spectral sensitivity of the material to the property change in interest is needed as well.

Facilities used for exposing materials in the laboratory are mostly based on the use of polychromatic radiation, i.e., radiation covering a broad range of wavelengths. Experiments

using this kind of radiation are designed to either simulate or accelerate naturally occurring ageing - the task which they usually complete well. In fewer studies, spectrally resolved radiation has been used in efforts pursuing the wavelength sensitivity of the materials (e.g., Watanabe et al., 1982; Trubiroha, 1989; Andradý et al., 1991; Andradý et al., 1992; Andradý et al., 1996; Searle, 2000; Chin et al., 2004; Trubiroha et al., 2004; Geburtig et al., 2010; Geburtig et al., 2011). The main challenges in these studies are related to the design of the facility, bounded by partly contradictory requirements. Both the wavelength resolution and the intensity levels of the exposing radiation are expected to be high enough, to be able to infer wavelength dependent property changes caused by exposures of reasonable durations.

This study reports on a facility designed and constructed for ageing materials with spectrally resolved UV radiation. The facility is based on a Xenon lamp as a source of radiation, and a spectrograph dividing the radiation into narrow bands of neighbouring wavelengths. The light emitted by the lamp mounted in a water-cooled lamp house is collected and collimated by a lense system. The beam is guided to travel through the filter filled with distilled water for removal of the infra-red part of the spectrum from the radiation. The beam is further guided onto the entrance slit, adjustable in width, of the spectrograph. Having entered the spectrograph, the beam is reflected onto a holographic flat-field grating which finally diffracts the beam and reflects the first order diffraction onto a planar sample exposure plane. The components of the facility are installed onto an optical breadboard of size 90 cm x 150 cm.

The facility was characterized by measuring the output of the spectrograph with a Bentham DM150 double monochromator spectroradiometer on ten equally spaced locations on the sample exposure plane. The irradiance on each location was found to be a narrow peak centering around a certain wavelength. The effective (center) wavelengths of the peaks ranged from 264 nm to 488 nm from one side of the sample plane towards the other. The FWHM (full width at half maximum) of the irradiance peaks, denoting the width of the band, was found to range from ~15 nm to ~5 nm, being broader at the shortest wavelengths. Narrowing the entrance slit width of the spectrograph proved to narrow the band widths and to decrease the maximum irradiances of the bands, as expected. The straylight rejection of the spectrograph was found to be of the order of 3-4 decades, being satisfactory for a single monochromator.

The ageing performance of the facility was tested by exposing samples of regular newspaper (43.9 g/m²) for 1, 2, 4, and 8 hours. The samples showed yellowing already after one-hour exposure, discernible by naked eye. On locations corresponding to irradiance peaks with effective wavelengths of 295 nm, 328 nm, and 358 nm, the yellowing appeared most pronounced, implying wavelength dependence in the yellowing sensitivity of the material. The yellowing was quantified by colour measurements carried out with a Minolta Chroma Meter CR-200 colorimeter on Yxy colour notation system. The measured coordinates were further used to calculate the yellowness index quantifying the actual phenomenon of yellowing. The calculated yellowness indices verified the wavelength dependence of photoyellowing already inferred by visual inspection of the exposed samples.

Additional performance tests were carried out with specimens made of polystyrene and rubber as stretched 10 % of its nominal width. The polystyrene sample showed measurable yellowing after 20 hours of exposure. In the rubber sample, noticeable cracking appeared after 600 hours of exposure. These findings verified the capability of the facility in ageing not only newspaper but also other types of polymeric materials within reasonable time frames.

The facility developed met the preset requirements. The radiant output on the sample exposure plane in terms of both the irradiance and the wavelength resolution proved applicable to its intended use for ageing materials with spectrally resolved UV radiation. The implementation differs from those previously reported especially in its compactness and efficiency. Indeed, the facility adds to the current technological know-how on artificial ageing of materials.

The facility finds several ways of use both in basic research on material ageing and photodegradation and in applied research aiming at, e.g., tailoring of wavelength selective protective additives for materials (see, e.g., Andrady, 2011). Specifically, it can be utilized in search of the action spectra, i.e., the generic wavelength sensitivities of materials to UV radiation.

3.5 Derivation of action spectrum of photoyellowing

The ability of UV radiation to cause photodegradation strongly depends on its energy, i.e., wavelength. It is therefore of vital importance to know the spectral distribution of the radiation exposing materials in a weathering experiment or in predicting the ageing behaviour of a material in its service environment. In addition, knowledge on the inherent wavelength sensitivity of the material is needed. In order to initiate photodegradation in a material, a photon has to be first absorbed by the material (Rabek, 1995). In essence, the wavelength sensitivity tells on which wavelengths the material is capable of absorbing photons, leading to a quantifiable change in the property of interest.

The wavelength dependence of the damage susceptibility may be described by a spectral response specific to the material and the type of damage. Two basic forms for the spectral response exist: an activation spectrum and an action spectrum (Trubiroha, 1989; Searle 2000). The distinction between those two forms lies on the principle followed in derivation of the response. The activation spectrum has been settled for a specific light source, and is therefore valid under exposure of that particular source. The action spectrum, also called as spectral or wavelength sensitivity, is derived by accounting for the radiant exposure used in the experiment, and is hence source-independent and applicable in any exposure conditions within certain limits.

Previously reported studies on spectral response of material to UV radiation have mainly yielded activation spectra applicable only in exactly the same exposure conditions as used for deriving the response. A few studies on the topic have resulted in action spectra - none of

which, however, have been universally applicable, but applicable to either certain duration or certain photon yield of exposure (e.g., Andradý, 1991).

In this study, a new approach to derive a generic action spectrum for one of the most usual manifestations of photodegradation, namely photoyellowing, is adopted. The method relies on exposure of the material with spectrally resolved radiation with known characteristics. Newspaper samples exposed for time periods of 1, 2, 4, and 8 hours have been analyzed for the change in their colour in several different locations on the sample, corresponding certain wavelengths of the exposing radiation. Yellowness indices computed from the measured colour coordinates are modelled applying a logarithmic model of the form

$$YI(\lambda_{eff}, t) = YI_0 \cdot \log_a [s(\lambda_{eff}) \cdot E(\lambda_{eff}) \cdot t + b], \quad (11)$$

where $YI(\lambda_{eff}, t)$ is the yellowness index measured at sample location corresponding effective wavelength of λ_{eff} , t is the duration of exposure, YI_0 is the yellowness index of an unexposed sample, $E(\lambda_{eff})$ is the irradiance exposing the sample on location corresponding to effective wavelength of λ_{eff} , and a , b , and $s(\lambda_{eff})$ are the parameters of the model, of which $s(\lambda_{eff})$ is the action spectrum searched for. A best solution for the equation was numerically found using a least squares fit.

The action spectrum obtained has inverse units of exposure, m^2J^{-1} , and reaches its maximum value $16.2 \mu\text{m}^2\text{J}^{-1}$ at the lowest considered wavelength of 264 nm, decreasing nonlinearly towards longer wavelengths and approaching zero at the upper limit of the considered wavelength range. The action spectrum may be assumed to represent the inherent wavelength-specific sensitivity of the material to photoyellowing. It is generic in the sense that it is independent from the duration or intensity of UV exposure, being therefore applicable in a range of different exposure conditions.

The significance of the study is its novel approach to a phenomenon of photodegradation. Instead of deriving an action spectrum for certain duration or intensity of exposure, the starting point for the modelling of the phenomenon is formulated in a way that it allows simultaneous inclusion of both dimensions of the accumulation of exposure: time and irradiance. The method may be expected suitable for deriving action spectra for the photoyellowing of other materials and possibly even action spectra of other damage types related to photodegradation.

4 Conclusions

The focus of this thesis has been on the methods used in investigation of the effects of UV radiation on materials. Suggestions for improved planning and conduction of an outdoor weathering test, more extensive quantification of the UV exposure on outdoor material samples, and more accurate characterization of UV radiation conditions prevailing in artificial weathering environments has been made. In addition, the design and construction of a novel facility for exposing materials with spectrally resolved UV radiation has been reported. Finally, a new approach for determining the action spectrum for one of the most common photodegradative phenomena, photoyellowing, has been proposed.

The study was initiated by developing a method for planning the timetable for an outdoor weathering programme in a way that the natural seasonal variability exhibited by the solar UV radiation is accounted for. The usefulness of the approach was analyzed by comparing the exposures predicted to accumulate over the adjusted weathering periods vs. periods with fixed durations. Application of the method increases the comparability of the test results obtained for a material weathered at different geographical locations with different rates of accumulation of total UV radiation exposure. The method may be applied for any period of time and for any location for which data on prevailing UV irradiance is available. Weathering experiments with exposure periods adjusted to the seasonal variations of local UV irradiance may be expected to yield more consistent data on the progress of the property changes in the material samples than experiments using exposure periods of fixed durations.

The study continued with a method applicable to patching the occasionally missing data in the time series of the measured UV irradiances. Complete time series is a necessity for derivation of total exposures accumulated onto the material samples over an exposure period. However, gaps in measured time series always appear to some extent due to laboratory calibrations, maintenance and malfunctions. To complete the time series for these gaps, a method for reconstruction of spectrally resolved solar UV irradiance at the Earth's surface was developed. The method is based on radiative transfer modeling with cloud optical depth inferred from the pyranometer measurements of global radiation within the wavelength range 300-3000 nm as input. The performance of the method was studied by a statistical analysis on the differences between reconstructed and measured daily spectral UV exposure. The results of the analysis proved the method applicable for the intended use in supplementing incomplete time series of measured daily spectral UV exposures.

The next step in this study dealt with UV exposure conditions in accelerated artificial weathering environments widely used in testing the durability of materials. A method for characterizing such conditions was developed. The method is based on spectrally resolved measurements of UV irradiance and a geometrical analysis of the radiation field prevailing in the exposure chamber. The total exposures accumulated onto the exposed material samples over the wavelength ranges of UV, UVA and UVB were analyzed in cases of lamps of different burning hours. Furthermore, the exposures were compared against those estimated to accumulate in natural outdoor circumstances from solar radiation. As a result, acceleration

factors linking the artificial and natural weathering conditions for their UV radiation stresses were derived. The acceleration factors were found to significantly depend on the wavelength range of UV radiation considered. The finding emphasized the need for knowledge on spectral distribution of UV radiation exposing materials in natural and artificial weathering tests as a prerequisite for the comparability of the results. Furthermore, it indicated the necessity of knowing the spectral sensitivity of the tested material for UV radiation induced damages, giving the impetus for the next part in this study.

A novel facility for ageing material with narrow-band UV radiation was designed and constructed in the next phase of the study, aiming at means to explore the wavelength dependencies in the damages caused by UV radiation in materials. The facility employs a Xenon arc lamp as a source of radiation and a spectrograph with a holographic flat-field grating to resolve the beam spectrally and reflect the spectrum onto a planar sample exposure plane. Analysis on the characteristic measurements of the radiant output of the facility proved the intensities high enough to enable ageing of samples within reasonable time frames. The performance of the facility was demonstrated through ageing samples of newspaper over time periods of different durations. The samples showed distinct patterns of photoyellowing, indicating certain dependence on wavelength. Furthermore, a clear logarithmic dependence between the exposure time and the degree of yellowing was found. These findings launched the work leading to the final part of this thesis.

The last part of the study emerged from the need to find a method to derive a universal action spectrum for the photoyellowing of a material. More generally, the aim was to develop a method to derive a material and damage specific action spectrum for any material exhibiting any kind of property change as a consequence of UV radiation exposure. The yellowing observed and quantified in newspaper samples exposed with the facility reported in the earlier part of this study was analyzed and modelled by employing a logarithmic formula. The model was found to yield an action spectrum of photoyellowing in a form independent from either duration or intensity and hence more universal than those formerly reported. The methodology developed opens a new pathway for the exploration of the wavelength dependencies in the susceptibility of materials to UV radiation induced damages and for determination of generic action spectra of property changes accompanying the ageing of materials.

References

- Alexandris, D., Varotsos, C., Ya Kondratyev, K. & Chronopoulos, G. 1999, "On the altitude dependence of solar effective UV", *Physics and Chemistry of the Earth, Part C: Solar, Terrestrial & Planetary Science*, vol. 24, no. 5, pp. 515-517.
- Allen, N.S., Edge, M., Ortega, A., Sandoval, G., Liauw, C.M., Verran, J., Stratton, J. & McIntyre, R.B. 2004, "Degradation and stabilisation of polymers and coatings: nano versus pigmentary titania particles", *Polymer Degradation and Stability*, vol. 85, no. 3, pp. 927-946.
- Andrady, A. 1997, "Wavelength sensitivity in polymer photodegradation", *Advances in Polymer Science, Polymer Analysis Polymer Physics*, Springer Berlin Heidelberg, pp. 47-94.
- Andrady, A.L., Hamid, S.H., Hu, X. & Torikai, A. 1998, "Effects of increased solar ultraviolet radiation on materials", *Journal of Photochemistry and Photobiology B: Biology*, vol. 46, no. 1-3, pp. 96-103.
- Andrady, A.L., Searle, N.D. & Crewdson, L.F.E. 1992, "Wavelength sensitivity of unstabilized and UV stabilized polycarbonate to solar simulated radiation", *Polymer Degradation and Stability*, vol. 35, no. 3, pp. 235-247.
- Andrady, A.L., Fueki, K. & Torikai, A. 1990, "Photodegradation of rigid PVC formulations. III. Wavelength sensitivity of the photo-yellowing reaction in processed PVC formulations", *Journal of Applied Polymer Science*, vol. 39, no. 3, pp. 763-766.
- Andrady, A.L., Fueki, K. & Torikai, A. 1991, "Spectral sensitivity of polycarbonate to light-induced yellowing", *Journal of Applied Polymer Science*, vol. 42, no. 7, pp. 2105-2107.
- Andrady, A.L., Hamid, H. & Torikai, A. 2011, "Effects of solar UV and climate change on materials", *Photochemical & Photobiological Sciences*, vol. 10, no. 2, pp. 292-300.
- Andrady, A., Song, Y., Parthasarathy, V., Fueki, K. & Torikai, A. 1991, "Photoyellowing of mechanical pulp. I. Examining the wavelength sensitivity of light-induced yellowing using monochromatic radiation", *Tappi Journal*, vol. 74, no. 8, pp. 162-168.
- Andrady, A.L., Torikai, A. & Kobatake, T. 1996, "Spectral sensitivity of chitosan photodegradation", *Journal of Applied Polymer Science*, vol. 62, no. 9, pp. 1465-1471.
- Anton-Prinet, C., Mur, G., Gay, M., Audouin, L. & Verdu, J. 1998, "Photoageing of rigid PVC—III. Influence of exposure conditions on the thickness distribution of photoproducts", *Polymer Degradation and Stability*, vol. 60, no. 2, pp. 283-289.
- Aphalo, P.J., Albert, A., Björn, L.O., McLeod, A., Robson, T.M., Rosenqvist, E. (eds.) 2012, *Beyond the Visible: A handbook of best practice in plant UV photobiology*, COST Action FA0906 UV4growth, University of Helsinki, Division of Plant Biology, Helsinki, 176 pp.
- Arola, A., Kaurola, J., Koskinen, L., Tanskanen, A., Tikkanen, T., Taalas, P., Herman, J., Krotkov, N. & Fioletov, V. 2003, "A new approach to estimating the albedo for snow - covered surfaces in the satellite UV method", *Journal of Geophysical Research: Atmospheres* (1984–2012), vol. 108, no. D17.

ASTM D1925–70 1970 (Reapproved 1988), Standard Test Method for Yellowness Index of Plastics, An American National Standard, American Society for Testing and Materials.

Baines, F.M., High UVB output mercury vapour lamps used in zoos: the Osram Ultra-Vitalux and Reptile UV Zoo Mega Ray mercury vapour lamps on test. Available: <http://www.uvguide.co.uk/zoolamps.htm> [2007, 12/15].

Blumthaler, M. 2004, "Quality assurance and quality control methodologies used within the Austrian UV monitoring network", Radiation Protection Dosimetry, vol. 111, no. 4, pp. 359-362.

Blumthaler, M. & Ambach, W. 1988, "Solar UVB-albedo of various surfaces", Photochemistry and photobiology, vol. 48, no. 1, pp. 85-88.

Blumthaler, M., Ambach, W. & Ellinger, R. 1997, "Increase in solar UV radiation with altitude", Journal of Photochemistry and Photobiology B: Biology, vol. 39, no. 2, pp. 130-134.

Blumthaler, M., Webb, A., Seckmeyer, G., Bais, A., Huber, M. & Mayer, B. 1994, "Simultaneous spectroradiometry: A study of solar UV irradiance at two altitudes", Geophysical Research Letters, vol. 21, no. 25, pp. 2805-2808.

Boersma, A. 2006, "Predicting the efficiency of antioxidants in polymers", Polymer Degradation and Stability, vol. 91, no. 3, pp. 472-478.

Bohren, C.F. & Clothiaux, E.E. 2006, Fundamentals of atmospheric radiation : an introduction with 400 problems, Wiley-VCH, Weinheim.

Boxhammer, J. 1999, "Current status of light and weather fastness standards, new equipment technologies, operating procedures and application of standard reference materials" in Weathering of plastics: testing to mirror real life performance, ed. G. Wypych, William Andrew Inc., ChemTec Publishing, Norwich (NY), pp. 43-60.

Brown, R. 1999, Handbook of polymer testing : physical methods, Marcel Dekker, New York (NY).

Bussiere, P., Gardette, J., Lacoste, J. & Baba, M. 2005, "Characterization of photodegradation of polybutadiene and polyisoprene: chronology of crosslinking and chain-scission", Polymer Degradation and Stability, vol. 88, no. 2, pp. 182-188.

Cahalan, R.F., Oreopoulos, L., Marshak, A., Evans, K.F., Davis, A.B., Pincus, R., Yetzer, K.H., Mayer, B., Davies, R. & Ackerman, T.P. 2005, "The I3RC: Bringing together the most advanced radiative transfer tools for cloudy atmospheres.", Bulletin of the American Meteorological Society, vol. 86, no. 9.

Chin, J.W., Martin, J. & Nguyen, T. 2001, "Effects of ultraviolet (UV) radiation" in Gap analysis for durability of fibre reinforced polymer composites in civil infrastructure, eds. V. Karbhari, J.W. Chin & R. Reynaud, American Society of Civil Engineering ASCE, pp. 80-99.

Chin, J., Byrd, E., Embree, N., Garver, J., Dickens, B., Finn, T. & Martin, J. 2004, "Accelerated UV weathering device based on integrating sphere technology", Review of Scientific Instruments, vol. 75, no. 11, pp. 4951-4959.

- Cho, J., Kim, H., Kim, Y. & Hong, J. 2003, "Dual curing of cationic UV-curable clear and pigmented coating systems photosensitized by thioxanthone and anthracene", *Polymer Testing*, vol. 22, no. 6, pp. 633-645.
- Chubarova, N.Y. & Nezval, Y.I. 2000, "Thirty year variability of UV irradiance in Moscow", *Journal of Geophysical Research: Atmospheres* (1984–2012), vol. 105, no. D10, pp. 12529-12539.
- CIE 1932, Commission internationale de l'Eclairage proceedings 1931, Cambridge University Press, Cambridge.
- Claudé, B., Gonon, L., Verney, V. & Gardette, J. 2001, "Consequences of photoageing on the durability of plastic glasses for automotive applications", *Polymer Testing*, vol. 20, no. 7, pp. 771-778.
- Den Outer, P., Slaper, H. & Tax, R. 2005, "UV radiation in the Netherlands: Assessing long - term variability and trends in relation to ozone and clouds", *Journal of Geophysical Research: Atmospheres* (1984 - 2012), vol. 110, no. D2.
- Farman, J.C., Gardiner, B.G. & Shanklin, J.D. 1985, "Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction", *Nature*, vol. 315, pp. 207-210.
- Feister, U. & Grewe, R. 1995, "Spectral albedo measurements in the UV and visible region over different types of surfaces", *Photochemistry and photobiology*, vol. 62, no. 4, pp. 736-744.
- Feister, U., Jäkel, E. & Gericke, K. 2002, "Parameterization of Daily Solar Global Ultraviolet Irradiation", *Photochemistry and photobiology*, vol. 76, no. 3, pp. 281-293.
- Feller, R.L. 1995, *Accelerated aging: photochemical and thermal aspects*, Getty Publications, The J. Paul Getty Trust, Edwards Bros., Ann Arbor (MI).
- Geburtig, A. & Wachtendorf, V. 2010, "Determination of the spectral sensitivity and temperature dependence of polypropylene crack formation caused by UV-irradiation", *Polymer Degradation and Stability*, vol. 95, no. 10, pp. 2118-2123.
- Geburtig, A., Kömmling, A. & Wachtendorf, V. 2011, "UV-LEDs - A new tool to determine the spectral response", CEEES Publication No. 15, *Natural and Artificial Ageing of Polymers*, 5th European Weathering Wymposium, 21st-23rd September 2011, Lisbon, Portugal. ed. T. Reichert, Gesellschaft für Umweltsimulation e.V. GUS, Karlsruhe, Germany, pp. 77-86.
- Green, A.E., Cross, K. & Smith, L.A. 1980, "Improved analytic characterization of ultraviolet skylight", *Photochemistry and photobiology*, vol. 31, no. 1, pp. 59-65.
- Grelier, S., Castellan, A. & Podgorski, L. 2007, "Use of low molecular weight modified polystyrene to prevent photodegradation of clear softwoods for outdoor use", *Polymer Degradation and Stability*, vol. 92, no. 8, pp. 1520-1527.
- Grenfell, T.C., Warren, S.G. & Mullen, P.C. 1994, "Reflection of solar radiation by the Antarctic snow surface at ultraviolet, visible, and near - infrared wavelengths", *Journal of Geophysical Research: Atmospheres*, vol. 99, no. D9, pp. 18669-18684.

- Gueymard, C. 1995, SMARTS2: a simple model of the atmospheric radiative transfer of sunshine: algorithms and performance assessment, Florida Solar Energy Center Cocoa, FL.
- Hanson, A.R. 2012, "What is colour?" in *Colour design : theories and applications*, ed. J. Best, Woodhead Publishing, Cambridge, pp. 3-23.
- Heikkilä, A., Tanskanen, A., Lindfors, A., Kärhä, P. & Syrjälä, S. 2007, "Quantification of material exposure to ultraviolet radiation", CEEES Publication No. 8, *Natural and Artificial Ageing of Polymers*, 3rd European Weathering Symposium, 12th-14th September 2007, Krakow, Poland, ed. T. Reichert, Gesellschaft für Umweltsimulation e.V. GUS, Karlsruhe, Germany, pp. 461-470.
- Herman, J.R., Bhartia, P.K., Torres, O., Hsu, C., Seftor, C. & Celarier, E. 1997, "Global distribution of UV-absorbing aerosols from Nimbus 7/TOMS data", *Journal of Geophysical Research: Atmospheres*, vol. 102, no. D14, pp. 16911-16922.
- Herman, J.R., Krotkov, N., Celarier, E., Larko, D. & Labow, G. 1999, "Distribution of UV radiation at the Earth's surface from TOMS-measured UV-backscattered radiances", *Journal of Geophysical Research: Atmospheres*, vol. 104, no. D10, pp. 12059-12076.
- Herman, J., Piacentini, R., Ziemke, J., Celarier, E. & Larko, D. 2000, "Interannual variability of ozone and UV - B ultraviolet exposure", *Journal of Geophysical Research: Atmospheres* (1984 - 2012), vol. 105, no. D23, pp. 29189-29193.
- ISO 21348:2007, *Space environment (natural and artificial) Process for determining solar irradiances*, ISO TC 20 SC 14 Space systems and operations, 5/3/2007.
- ISO/CIE 1999, *Erythema reference action spectrum and standard erythema dose ISO 17166:1999(E) CIE S 007/E-1998*, CIE Central Bureau, Vienna.
- Jacques, L. 2000, "Accelerated and outdoor/natural exposure testing of coatings", *Progress in polymer science*, vol. 25, no. 9, pp. 1337-1362.
- Kaczmarek, H., Ołdak, D., Malanowski, P. & Chaberska, H. 2005, "Effect of short wavelength UV-irradiation on ageing of polypropylene/cellulose compositions", *Polymer Degradation and Stability*, vol. 88, no. 2, pp. 189-198.
- Karbhari, V., Chin, J.W. & Reynaud, R. 2001, "Gap analysis for durability of fibre reinforced polymer composites in civil infrastructure", CERF, American Society of Civil Engineers, USA.
- Klemann, B.M. 2003, "Correlations between xenon arc accelerated weathering tests and outdoor weathering", NIP & Digital Fabrication Conference, 2003 International Conference on Digital Printing Technologies Society for Imaging Science and Technology, New Orleans (LA), September 28, 2003, pp. 406.
- Koller, L.R. 1965, *Ultraviolet radiation*, 2nd ed., John Wiley & Sons Inc., New York (NY).
- Kylling, A., Persen, T., Mayer, B. & Svenøe, T. 2000, "Determination of an effective spectral surface albedo from ground - based global and direct UV irradiance measurements", *Journal of Geophysical Research: Atmospheres* (1984 - 2012), vol. 105, no. D4, pp. 4949-4959.

- Kylling, A., Stamnes, K. & Tsay, S. 1995, "A reliable and efficient two-stream algorithm for spherical radiative transfer: Documentation of accuracy in realistic layered media", *Journal of Atmospheric Chemistry*, vol. 21, no. 2, pp. 115-150.
- Lakkala, K., Arola, A., Heikkilä, A., Kaurola, J., Koskela, T., Kyrö, E., Lindfors, A., Meinander, O., Tanskanen, A. & Gröbner, J. 2008, "Quality assurance of the Brewer spectral UV measurements in Finland", *Atmospheric Chemistry and Physics*, vol. 8, no. 13, pp. 3369-3383.
- Lenoble, J. 1993, *Atmospheric radiative transfer*, A. Deepak Publishing, Hampton (VA).
- Liauw, C., Childs, A., Allen, N., Edge, M., Franklin, K. & Collopy, D. 1999, "Effect of interactions between stabilisers and silica used for anti-blocking applications on UV and thermal stability of polyolefin film 2. Degradation studies", *Polymer Degradation and Stability*, vol. 65, no. 2, pp. 207-215.
- Lindfors, A., Kaurola, J., Arola, A., Koskela, T., Lakkala, K., Josefsson, W., Olseth, J.A. & Johnsen, B. 2007, "A method for reconstruction of past UV radiation based on radiative transfer modeling: Applied to four stations in northern Europe", *Journal of Geophysical Research: Atmospheres* (1984–2012), vol. 112, no. D23.
- Liou, K.N. 2002, *An introduction to atmospheric radiation*, 2nd ed., Academic Press, Amsterdam.
- Lund Myhre, C. & Nielsen, C.J. 2004, "Optical properties in the UV and visible spectral region of organic acids relevant to tropospheric aerosols", *Atmospheric Chemistry and Physics*, vol. 4, no. 7, pp. 1759-1769.
- Madronich, S. 1993, "The atmosphere and UV-B Radiation at Ground Level" in *Environmental UV photobiology*, eds. A.R. Young, L.O. Björn, J. Moan & W. Nultsch, Plenum Press, New York (NY), pp. 1-39.
- Masters, L.W. & Bond, L.F. 1999, "Choices in the design of outdoor weathering tests" in *Weathering of plastics: testing to mirror real life performance*, ed. G. Wypych, William Andrew Inc., ChemTec Publishing, pp. 15-27.
- Mayer, B. & Kylling, A. 2005, "Technical note: The libRadtran software package for radiative transfer calculations-description and examples of use", *Atmospheric Chemistry and Physics*, vol. 5, no. 7, pp. 1855-1877.
- Mayer, B., Seckmeyer, G. & Kylling, A. 1997, "Systematic long - term comparison of spectral UV measurements and UVSPEC modeling results", *Journal of Geophysical Research: Atmospheres* (1984 - 2012), vol. 102, no. D7, pp. 8755-8767.
- McGreer, M. 2001, *Weathering Testing Guidebook*, Atlas Electric Devices Company Pub. No. 2062/098/200/AA/03/01, Atlas Material Testing Solutions, USA.
- McKenzie, R.L., Björn, L.O., Bais, A. & Ilyasd, M. 2003, "Changes in biologically active ultraviolet radiation reaching the Earth's surface", *Photochemical & Photobiological Sciences*, vol. 2, no. 1, pp. 5-15.

- McKenzie, R., Kotkamp, M. & Ireland, W. 1996, "Upwelling UV spectral irradiances and surface albedo measurements at Lauder, New Zealand", *Geophysical Research Letters*, vol. 23, no. 14, pp. 1757-1760.
- McPeters, R.D., Bhartia, P., Krueger, A.J., Herman, J.R., Wellemeyer, C.G., Seftor, C.J., Jaross, G., Torres, O., Moy, L. & Labow, G. 1998, "Earth probe total ozone mapping spectrometer (TOMS): data products user's guide", Technical Publication 1998-206895, National Aeronautics and Space Administration, Goddard Space Flight Center, Greenbelt (MD), 64 pp.
- Neumann, M.G., Schmitt, C.C., Catalina, F. & Goi, B.E. 2007, "The relation between the polymerization rates and swelling coefficients for copolymers obtained by photoinitiation", *Polymer Testing*, vol. 26, no. 2, pp. 189-194.
- Peinado, C., Allen, N., Salvador, E.F., Corrales, T. & Catalina, F. 2002, "Chemiluminescence and fluorescence for monitoring the photooxidation of an UV-cured aliphatic polyurethane-acrylate based adhesive", *Polymer Degradation and Stability*, vol. 77, no. 3, pp. 523-529.
- Piazena, H. 1996, "The effect of altitude upon the solar UV-B and UV-A irradiance in the tropical Chilean Andes", *Solar Energy*, vol. 57, no. 2, pp. 133-140.
- Pickett, J. & Gardner, M. 2005, "Reproducibility of Florida weathering data", *Polymer Degradation and Stability*, vol. 90, no. 3, pp. 418-430.
- Pickett, J.E., Gardner, M.M., Gibson, D.A. & Rice, S.T. 2005, "Global weathering of aromatic engineering thermoplastics", *Polymer Degradation and Stability*, vol. 90, no. 3, pp. 405-417.
- Rabek, J.F. 1995, *Polymer photodegradation : mechanisms and experimental methods*, Chapman & Hall, London.
- Rivaton, A., Mailhot, B., Robu, S., Lounaci, M., Bussière, P. & Gardette, J. 2006, "Photophysical processes and photochemical reactions involved in poly-(*N*-vinylcarbazole) and in copolymers with carbazole units", *Polymer Degradation and Stability*, vol. 91, no. 3, pp. 565-572.
- Sabaa, M. & Mokhtar, S. 2002, "Chemically induced graft copolymerization of itaconic acid onto cellulose fibers", *Polymer Testing*, vol. 21, no. 3, pp. 337-343.
- Searle, N.D. 2000, "Activation spectra: techniques and applications to stabilization and stability testing of materials" in *Durability 2000: accelerated and outdoor weathering testing*, eds. W.D. Ketola & J.D. Evans, ASTM International, pp. 41-58.
- Searle, N.D. 2003, "Environmental effects on polymeric materials" in *Plastics and the Environment*, ed. A.L. Andrady, John Wiley & Sons, John Wiley & Sons Inc., Hoboken (NJ), pp. 313-358.
- Searle, N., Giesecke, P., Kinmonth, R. & Hirt, R. 1964, "Ultraviolet spectral distributions and aging characteristics of xenon arcs and filters", *Applied Optics*, vol. 3, no. 8, pp. 923-927.
- Seckmeyer, G., Bais, A., Bernhard, G., Blumthaler, M., Booth, C.R., Disterhoft, P., Eriksen, P., McKenzie, R.L., Miyauchi, M. & Roy, C. 2001, *Instruments to measure solar ultraviolet*

radiation, Part 1: Spectral instruments. Global Atmosphere Watch Publication, GAW Report No. 125, WMO TD No. 1066, World Meteorological Organization, Geneva.

Seckmeyer, G., Bais, A., Bernhard, G., Blumthaler, M., Booth, C., Lantz, K., McKenzie, R., Disterhoft, P. & Webb, A. 2005, Instruments to measure solar ultraviolet radiation, Part 2: Broadband instruments measuring erythemally weighted solar irradiance. Global Atmosphere Watch Publication, GAW Report No. 164, WMO TD No. 1289, World Meteorological Organization, Geneva.

Seckmeyer, G., Bais, A., Bernhard, G., Blumthaler, M., Druke, S., Kiedron, P., Lantz, K., McKenzie, R., Riechelmann, S. & Kouremeti, N. 2010, Instruments to measure solar ultraviolet radiation, Part 4: array spectroradiometers. Global Atmosphere Watch Publication, GAW Report No. 191, WMO TD No. 1538, World Meteorological Organization, Geneva.

Seckmeyer, G., Bais, A., Bernhard, G., Blumthaler, M., Johnsen, B., Lantz, K. & McKenzie, R. 2010, Instruments to measure solar ultraviolet radiation, Part 3: Multi-channel filter instruments. Global Atmosphere Watch Publication, GAW Report No. 190, WMO TD No. 1537, World Meteorological Organization, Geneva.

Seckmeyer, G., Pissulla, D., Glandorf, M., Henriques, D., Johnsen, B., Webb, A., Siani, A., Bais, A., Kjeldstad, B. & Brogniez, C. 2008, "Variability of UV irradiance in Europe", *Photochemistry and photobiology*, vol. 84, no. 1, pp. 172-179.

Shanmugaraj, A., Kim, J.K. & Ryu, S.H. 2005, "UV surface modification of waste tire powder: characterization and its influence on the properties of polypropylene/waste powder composites", *Polymer Testing*, vol. 24, no. 6, pp. 739-745.

Sthel, M., Rieumont, J. & Martinez, R. 1999, "Testing a furfuryl alcohol resin as a negative photoresist", *Polymer Testing*, vol. 18, no. 1, pp. 47-50.

Tanskanen, A. & Lindfors, A. 2008, Methodology of the PROMOTE Integrated UV Record Service, http://promote.fmi.fi/Documents/UVRecordService_methodology.pdf.

Trubiroha, P. 1989, "The spectral sensitivity of polymers in the spectral range of solar radiation" in *Advances in the stabilization and controlled degradation of polymers*, vol. 1, ed. A.V. Patsis, Technomic Publishing Company, Inc., pp. 236-241.

Trubiroha, P., Geburtig, A., Wachtendorf, V. 2004, "Proceedings 3rd international symposium on service life prediction", *Determination of the spectral response of polymers*, eds. J.M. Ryntz, R.A. Dickie & R.A. Martin, Federation of Societies for Coatings Technology, Sedona (AZ), pp. 241.

Udelhofen, P.M., Gies, P., Roy, C. & Randel, W.J. 1999, "Surface UV radiation over Australia, 1979–1992: Effects of ozone and cloud cover changes on variations of UV radiation", *Journal of Geophysical Research: Atmospheres* (1984–2012), vol. 104, no. D16, pp. 19135-19159.

UNEP 1998, United Nations Environment Programme, Environmental Effects Assessment Panel 1998, "Environmental effects of ozone depletion: 1998 assessment", *Journal of Photochemistry and Photobiology B: Biology*, vol. 46, no. 1–3, pp. 1-108.

UNEP 2003, United Nations Environment Programme, Environmental Effects Assessment Panel 2003, "Environmental effects of ozone depletion and its interactions with climate change: 2002 assessment", Photochemical & Photobiological Sciences, vol. 2, no. 1, pp. 1-72.

UNEP 2012, United Nations Environment Programme, Environmental Effects Assessment Panel 2012, "Environmental effects of ozone depletion and its interactions with climate change: progress report, 2011", Photochemical & Photobiological Sciences, vol. 11, no. 1, pp. 13-27.

Young, A.R., Björn, L.O., Moan, J. & Nultsch, W. cop. 1993, Environmental UV photobiology, Plenum Press, New York (NY), pp. 1-39.

Watanabe, M., Furuya, M., Miyoshi, Y., Inoue, Y., Iwahashi, I. & Matsumoto, K. 1982, "Design and performance of the Okazaki Large Spectrograph for photobiological research", Photochemistry and photobiology, vol. 36, no. 4, pp. 491-498.

Webb, A.R. 1998, UVB instrumentation and applications, OPA (Overseas Publishers Association) Amsterdam B.V., Amsterdam, The Netherlands.

Webb, A.R., Gardiner, B.G., Leszczynski, K., Mohnen, V., Johnston, P., Harrison, N. & Bigelow, D. 2003, Quality Assurance in Monitoring Solar Ultraviolet Radiation: the State of the Art, World Meteorological Organization, Global Atmosphere Watch Publication, GAW Report No. 191, WMO TD No. 1180, World Meteorological Organization (WMO), Geneva.

Webb, A.R., Gardiner, B.G., Martin, T.J., Leszczynski, K., Metzdorf, J. & Mohnen, V.A. 1998, Guidelines for site quality control of UV monitoring, Global Atmosphere Watch Publication, GAW Report No. 126, TD No. 884, World Meteorological Organization (WMO), Geneva.

Wypych, G. 1999, Weathering of plastics : testing to mirror real life performance, William Andrew Inc., ChemTec Publishing, Norwich (NY).

Wypych, G. & Faulkner, T. 1999, "Basic parameters in weathering studies" in Weathering of plastics: testing to mirror real life performance, ed. G. Wypych, William Andrew Inc., ChemTec Publishing, pp. 1-13.

Zerefos, C., Balis, D., Bais, A., Gillotay, D., Simon, P., Mayer, B. & Seckmeyer, G. 1997, "Variability of UV - B at four stations in Europe", Geophysical Research Letters, vol. 24, no. 11, pp. 1363-1366.